TECHNOLOGY

ANALYTICAL ABSTRACTS

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

2295. **Some problems of subdivision of samples for chemical analysis.** H. Kamada (*Japan Analyst*, 1953, **2** [4], 331–334).—The fluctuation of the results of chemical analysis due to different methods of subdivision of the primary sample was closely examined and statistically analysed. Errors caused by an improper subdivision of the sample are generally greater than those introduced by the analytical procedures, especially for substances like coal, coke, ores and industrial intermediates. The quartering method was compared with the increment method (B.S. 1017:1942) and found not to be an improvement, in spite of its tedious procedure. K. SAITO

2296. **The theoretical basis of "sensitivity tests" and their application to some potential organic reagents for metals.** H. Irving and H. S. Rossotti (*Analyst*, 1955, **80**, 245–260).—Some factors determining the analytical usefulness of a reagent are discussed theoretically, particularly the changes involved in modifications of the structure of a reagent of low selectivity, *i.e.*, 8-hydroxyquinoline. The results of "sensitivity tests" with 33 cations on 8-hydroxycinnoline (**I**), 8-hydroxyquinazoline (**II**) and its 2:4-dimethyl derivative (**III**), and 5:8-dihydroxy-2:3-dimethylquinoxaline (**IV**) are tabulated and discussed. **I** and **II** (as well as 5-hydroxyquinoxaline) are more selective but less sensitive (except with some cations) than oxine. The behaviour of **III** is similar to that of **II**, but less selective. In general, these reagents do not appear to have any striking analytical advantage over oxine. If the stability constants and relevant physical properties of each complex were known, the analytical value of a reagent could be predicted. In practice, insufficient data are available and theoretical equations are often complicated by factors such as competitive complex-formation. Hence sensitivity tests, although of limited value, appear to be the best approach to the discovery of the potentialities of a reagent. A. O. JONES

2297. **An investigation of 5-nitroso-oxine as an analytical reagent.** H. Irving, R. G. W. Hollingshead and G. Harris (*Analyst*, 1955, **80**, 260–261).—Results of sensitivity tests with 5-nitroso-oxine suggested that it should be a more selective reagent than oxine, since it gave no ppt. with Al and did not form insoluble complexes with Ga, In or Hg, but it gave unsatisfactory results with the common metals. Even with Cu^{++}, pptn. under optimum conditions yielded results ranging from 89·5 to 98·5 per cent. of the theoretical in replicate determinations, indicating poor reproducibility and incomplete pptn. With Zn, results were still less satisfactory, never exceeding 75 per cent. of the theoretical. Attempts to improve the condition of the ppt. by hot digestion or use of hot ammoniacal solutions at pH 7 to 9 led only to the formation of a dark compound which, on ultimate analysis, did not correspond to any definite formula. Reasons for the behaviour of the reagent are suggested from a study of its absorption spectrum, dissociation constants and its inertness towards Br. A. O. JONES

2298. **8-Hydroxy-5-methyl-7-nitrosoquinoline and its sensitivity and selectivity towards certain metallic ions.** R. G. W. Hollingshead (*Anal. Chim. Acta*, 1955, **12** [3], 201–210).—8-Hydroxy-5-methyl-7-nitrosoquinoline (prep. described) yields precipitates with the ions of a number of metals in low concn. and at various pH values. As a reagent for these metals it is a little more sensitive than 8-hydroxyquinoline, but shows a similar lack of selectivity. These properties are discussed in relation to other derivatives of 8-hydroxyquinoline. W. C. JOHNSON

2299. **Hydroxyaldimines and hydroxyketimines as organic precipitants.** A. K. Mukherjee (*Z. anal. Chem.*, 1955, **145** [5], 321–324).—The qual. reactions of various metal ions with 2:4-dihydroxybenzaldehyde, 2-hydroxy-1-naphthaldehyde (**I**) and *o*-hydroxyacetophenone (**II**) in both aq. NH_3 and methylamine solutions are tabulated. The pptn. of Cu and Ni from aqueous solutions with **I** and **II** in methylamine was quant. The ppt. are unstable in acid solution, and are insol. in water and in high concn. of aq. NH_3 or methylamine. These reactions are well suited for the detection of small amounts of a number of metal ions in aq. soln. R. STERN

2300. **Uses of thiocarbohydrazide in analytical chemistry.** C. Duval and Tran Ba Loc (*Compt. Rend.*, 1955, **240** [10], 1097–1099).—Thiocarbohydrazide (**I**), prepared by condensation of CS_2 (1 mol.) with hydrazinium hydroxide (2 mol.) (*cf. Ber. dtsch. chem. Ges.*, 1908, **41**, 1099), can be used, as a 0·5 per cent. solution in H_2O or aq. ethanol (3 + 1), for qual. and quant. analyses. Distinctive spot-tests (coloration or pptn.) for certain metal ions are listed and are valid for paper partition chromatography. Aldehydes can be identified and determined because they react quant. with **I** yielding coloured hydrazones (m.p. ill-defined), each having a characteristic thermolysis curve. A separation of Mo from W and U can be effected by pptn., in the cold at pH 2, of a maroon Mo - **I** complex (**II**), which is easily sol. in a (1 + 2) mixture of acetone and *n*-butanol forming a stable brown soln. that obeys Beer's law at $\simeq$ 400 mμ; neither W nor U is pptd. under these conditions. This procedure is useful for removing Mo during the colorimetric determination of U by the thiocyanate method. Molybdenum can be determined, either photometrically in the brown soln. if > 15 μg per ml are present, or gravimetrically by igniting **II** to const. wt. (MoO_3) at 500° C (the ppt. is removed by centrifuging or selective micro-extraction, and washed with 1 per cent. HCl). For molybdenum contents of 70 to 80 mg the error is from $-1·3$ to

+ 0·2 per cent., whether or not W and U are present. W. J. BAKER

2301. **Iron (II) perchlorate as a reductant in glacial acetic acid.** O. N. Hinsvark and K. G. Stone (*Anal. Chem.*, 1955, **27** [3], 371–373).—The sensitivity and stability of $Fe(ClO_4)_2$ in glacial acetic acid as a volumetric reducing agent are examined. Soln. of $NaMnO_4$ and CrO_3 in glacial acetic acid are determined amperometrically with platinum-wire electrodes under N, the sensitivity at the equivalence point being increased by addition of 70 per cent. $HClO_4$ (0·5 ml) and application of a 150-mV potential. The results of 15 specimen determinations are presented. D. A. PANTONY

2302. **Qualitative analysis by the use of an anion-exchange resin.** K. Takiyama and E. Suito (*Japan Analyst*, 1955, **4** [1], 8–11).—The application of the anion-exchange resin Amberlite IRA-410 to group separation was studied. The sample soln. containing common cations is passed successively through columns of the resin in various anion forms (Cl', S'', OH', CO_3'', etc.). The production of precipitates may lead to colloidal soln., which makes filtration difficult; this defect can be avoided by adjusting the concn. of the sample soln. (0·01 to 0·1 *M*) and the velocity of the flow ($\simeq$ 10 ml per min.). The influence of PO_4''' and organic acid radicles on the group separation is completely eliminated.
K. SAITO

2303. **Recovery of chloroform used in dithizone extraction.** J. B. Mullin and J. P. Riley (*Analyst*, 1955, **80**, 316–317).—Recovery of $CHCl_3$ from dithizone reagent for re-use is often difficult owing to formation of oxidation and decomposition products of $CHCl_3$ (*e.g.*, phosgene), which oxidise dithizone to diphenylthiocarbodiazone. These contaminants can be removed by the action of Na_2SO_3. *Procedure*—The $CHCl_3$ is distilled through a layer of 10 per cent. Na_2SO_3 soln. The distillate is shaken either with 3 per cent. hydroxylamine hydrochloride soln. or with portions of 10 per cent. Na_2SO_3 soln. until the aq. phase is colourless. The $CHCl_3$ is then re-distilled from CaO or activated charcoal into about 1 per cent. of its vol. of freshly distilled ethanol. With very badly contaminated samples a second re-distillation may be necessary.
A. O. JONES

2304. **Analytical applications of sensitivity diagrams. II. Investigation of impurities in primary standards for acid - base titrations.** F. Burriel-Martí, J. Ramirez-Muñoz and R. Escobar-Godoy (*Inf. Quím. Anal.*, 1955, **9** [2], 39–52).—The significance of impurities in primary standards, and their determination, particularly with the aid of sensitivity diagrams, are discussed, with special reference to borax as a standard. L. A. O'NEILL

2305. **Mixed indicator for complexiметric titrations.** K. Gerlach (*Angew. Chem.*, 1955, **67** [6], 178).—The addition of dimethyl yellow or methyl orange to Eriochrome black T indicator is recommended for titrations with EDTA (*e.g.*, determination of Mg) in alkaline medium. The colour change is from grey to wine-red. S.C.I. ABSTR.

2306. **Amperometric titration of solutions of some heavy metals with sodium hydroxide solution using a rotating platinum electrode.** J. Kamecki and M. Slabon (*Roczn. Chem.*, 1955, **29** [1], 107–114).—The apparatus used is described in some detail. The rotating electrode comprises a platinum wire protruding 5 mm out of the glass tube in which it is sealed and which is rotated at 1000 to 1500 r.p.m. For the second electrode, a saturated calomel electrode is used. A diagram of the circuit is given. The measurements are carried out by covering the rotating electrode with a known vol. of the soln. concerned, establishing a suitable current in the circuit and observing its change with the amount of alkali added. This method can be applied to titrations of $\simeq$ 0·1 *N* solutions (diluted to $\simeq$ 0·02 *N* for use) of ferric nitrate, copper sulphate, zinc chloride and lead nitrate with *N* NaOH soln.; details are given. Results are tabulated and graphically represented, the breaks in the plot of current against vol. of NaOH added giving the equivalence points. Satisfactory results were obtained, except with $Pb(NO_3)_2$, when they were too low. In all cases, however, best results are given at different electrolytic optima, and though the platinum electrode can be used connected to either pole of the accumulator, good results (error < 1 per cent.) are obtained when it is joined to the positive pole. A. O. JAKUBOVIC

2307. **Mercury - mercurous acetate indicator electrode for potentiometric titrations in anhydrous acetic acid.** E. Scarano and A. Ceglie (*Anal. Chim. Acta*, 1955, **12** [3], 292–299).—A gold wire is sheathed in a glass tube and bears at one end a gold plate 2 to 3 mm in diameter. Mercury is deposited electrolytically on the plate and the mercury is then covered with a layer of mercurous acetate by electrolysis in *N* acetic acid. The acetate layer becomes thinner, and eventually broken, in use, and the electrode should be prepared fresh for each titration. The electrode is used, with an S.C.E. and a saturated potassium chloride - agar bridge, for the titration of anhydrous acetic acid solutions of potassium hydrogen phthalate and Na_2CO_3 with 0·1 *N* $HClO_4$ in anhydrous acetic acid. W. C. JOHNSON

2308. **Some titrations by the "dead-stop" method with mercury electrodes.** H. L. Kies (*Anal. Chim. Acta*, 1955, **12** [3], 280–284).—Various titrations are performed according to a "dead-stop" electrometric principle previously described (*Anal. Chim. Acta*, 1954, **10**, 575; **11**, 382), with the use of a pair of mercury electrodes having a p.d. of several mV. Mercuric ions, in a base electrolyte containing NaOH and Na_2SO_3, are titrated with $FeCl_2$ soln.; Cl' or Br', in a base electrolyte containing $NaNO_3$ and HNO_3, are titrated with $HgNO_3$, $HgClO_4$ or $AgNO_3$ soln.; alternatively, a Hg' soln. can be titrated with NaCl soln. A known amount of Hg' is titrated with I' or SCN' in order to determine these anions; I' can also be titrated with Ag' or *vice versa*. Cyanide, in a soln. of KOH, $NaNO_3$ and KBr, is titrated with Hg'' soln., or the CN' soln. is added from a burette to a Hg' soln. containing $NaNO_3$ and slightly acidified with HNO_3. W. C. JOHNSON

2309. **Quantitative electrolytic generation of permanganate ions.** P. S. Tutundžić and S. Mladenović (*Anal. Chim. Acta*, 1955, **12** [4], 382–389).—The generation of MnO_4' by the electrolysis of an acid soln. of $MnSO_4$ is investigated with a view to its quant. application in coulometry. The conditions under which O, MnO_2 and MnO_4' are produced at a platinum anode are first considered from a theoretical standpoint. A practical investigation shows that for the quant. generation of MnO_4' the anolyte should consist of 0·02 to 0·45 *M*

$MnSO_4$, 3·6 *N* with respect to H_2SO_4; the anode potential should be + 1·4 V. The cathelyte is a soln. of 5 ml of conc. H_2SO_4 and 5 g of K_2SO_4 in 95 ml of water. W. C. JOHNSON

2310. **Coulometric permanganometric determination of oxalate, ferrous iron and arsenite.** P. S. Tutundžić and Sreten Mladenović (*Anal. Chim. Acta*, 1955, **12** [4], 390–399).—The conditions already determined (see *Anal. Abstr.*, 1955, **2**, 2309) for the quant. electrolytic generation of MnO_4' are used in the coulometric titration of oxalate, $Fe^{\cdot\cdot}$ and AsO_3'''. A current of 7 to 20 mA, providing a current intensity of 1·2 to 3·4 mA per cm^2, is used for 1 to 8-mg quantities of each ion. The anode potential is + 1·45 to + 1·62 V *vs.* the normal hydrogen electrode and the titrations are completed in 5 to 20 min. An indicator soln. is prepared by mixing 4 ml of 0·025 *M* *o*-phenanthroline - $FeSO_4$ with 4 ml of 0·1 *N* $Fe(NH_4)_2(SO_4)_2$ and 30 ml of water. Oxalate (2 to 10 mg in 60 ml of anolyte) is titrated at 30° C. Since the indicator is oxidised more readily than the oxalate it is not added until the oxalate is completely oxidised and an excess of MnO_4' remains. An excess (1 ml) of the indicator soln. is added and the passage of current is continued until the indicator colour changes. A separate titration of 1 ml of the indicator soln. in the same anolyte provides the necessary correction. The max. errors are + 0·93 and − 0·85 per cent. Ferrous ions are titrated similarly, but the indicator soln. (2 to 3 drops) is added first to the anolyte and is titrated to obtain the appropriate correction; the Fe^{II} soln. is then added and titrated. The max. errors for $Fe^{\cdot\cdot}$ are + 1·11 and − 0·47 per cent. In the titration of AsO_3''', the electrolysis is continued at a temp. of 30° to 50° C until an excess of MnO_4' remains after stirring the soln. for 10 min. with the current interrupted; 1 ml of the indicator soln. is then added and the titration is completed. The max. errors are + 0·62 and − 0·87 per cent. W. C. JOHNSON

2311. **The use of a thallic - thallous system as a pH indicator.** E. Rancke-Madsen and T. Kjærgård (*Acta Chem. Scand.*, 1955, **9** [2], 293–298).—It is shown that the thallic - thallous redox system can, on addition of KI and starch, be used as a pH indicator with two transition levels in the pH scale, one of which is clear, reproducible and reversible. The transitions take place within a narrow pH range. This system can be used as an indicator in the titration of CO_3'' as a univalent base. O. M. WHITTON

2312. **Inorganic chromatography on paper; separation of mercury, lead, copper, bismuth and cadmium.** R. Indovina, E. De Leo and B. M. Ricotta (*Ann. Chim., Roma*, 1955, **45** [2–3], 244–247).—Separation of the cations of Hg, Pb, Cu, Bi and Cd is achieved with the mixture butanol - acetic acid - 12 *N* HCl - water, with ascending paper chromatography. The spots are developed with dithizone. R_F values and the colours obtained are tabulated. C. A. FINCH

2313. **Spray reagent for identification of organic acids.** S. M. Martin (*Chem. & Ind.*, 1955, [16], 427–428).—A system of three sprays (potassium ferrocyanide, ferric ammonium sulphate and aq. NH_3 soln.) is used for identifying acids of similar R_F values. Chromatograms of organic acid spots on washed filter-paper were developed in either butanol - ethanol - formic acid - water (10:2:2:2) or pyridine - aq. NH_3 soln. - H_2O (6:2:1). The dried chromatograms were first heavily sprayed with aq. 10 per cent. w/v potassium ferrocyanide and, after being dried, re-sprayed with 0·5 per cent. w/v ferric ammonium sulphate in 70 per cent. ethanol. Spots were then marked and colours noted. After the chromatogram had been heated for 5 to 10 min. at 100° C, the changed background colours were bleached with 10 per cent. (w/v) ammonia soln. and colour readings were taken at intervals of 1 to 3 days. The colour reactions of 18 test compounds (*e.g.*, aconitic, citric, malic, oxalic and succinic acids) are tabulated. S.C.I. ABSTR.

2314. **The application of the iodine - azide reaction to paper chromatograms.** W. Awe, I. Reinecke, J. Thum, F. Newald and G. A. Ulex (*Naturwissenschaften*, 1954, **41** [22], 528).—The iodine - azide reaction is catalysed by sulphur ions and increases in speed with their increasing concentration. In the authors' experience substances containing S–S bridges (cystine) or thioethers (methionine) or thiazoles (vitamin B_1) can act as catalysts. That these substances may be broken down as the result of their catalytic action seems likely. The test if carefully employed is useful as a guide. For the identification of sulphur-containing amino acids the paper should be sprayed with iodine - azide reagent (1 g of NaN_3 in 100 ml of 0·005 *N* I) and immediately afterwards with starch solution. The same technique can be used for penicillin and will reveal 5 μg of the antibiotic on paper. E. KAWERAU

2315. **Gas - liquid partition chromatography.** D. Harvey and D. E. Chalkley (*Fuel, Lond.*, 1955, **34** [2], 191–200).—Methods of gas chromatography are reviewed. Two disadvantages of the method of displacement from charcoal are discussed. The technique of gas - liquid partition chromatography and its use for qual. and quant. analysis are described. New features devised by the authors are a method of introducing a gas sample, the use of triethanolamine for separating NH_3 and the methylamines, and the use of glycerol for separating alcohols, ketones and ethers in the presence of water. A. B. DENSHAM

2316. **Inorganic chromatography on rotating discs.** R. Indovina and B. M. Ricotta (*Ann. Chim., Roma*, 1955, **45** [2–3], 241–243).—The rotating-paper-disc method of Caronna (*Anal. Abstr.*, 1955, **2**, 2256), with a range of solvents, is used to separate the cations of Cu, Cd, Bi and Hg. Chromatograms are rapidly obtained and provide clear identification of the cations. R_F values for different solvent mixtures, using fixed and rotating discs, are tabulated. C. A. FINCH

2317. **Electrochromatography. V. Separation of inorganic cations by formation of complex ions.** M. Maki (*Japan Analyst*, 1955, **4** [1], 21–25).—The separation of cations by electrochromatography (200 V, 4 to 9 mA, 4 hr.) was studied in mixed soln. of ethylenediamine (0·1 *M*) - NH_4 tartrate (0·1 *M*) and triethanolamine (0·1 *M*) - NH_4 tartrate (0·1 *M*). Ions that form cationic complexes with amines and those that form anionic complexes with tartrate can be separated efficiently. The mobility of ions can be modified by changing either the molar ratio of the complex-forming reagents or the concn. of one of the components. The use of $Na_4P_2O_7$ as a complex-forming reagent was also studied and a significant influence of the pH value

of the soln. on the mobility of ions was observed. The separation of spots of ion groups, which is otherwise difficult (*e.g.*, As''' - Sb'' - Sn'', Al''' - Fe''', Ca'' - Sr'' - Ba'' - Mg''), can be achieved by this method. K. SAITO

2318. **Effect of concentration and sorption upon migration of cations in paper electrochromatography.** T. R. Sato, W. P. Norris and H. H. Strain (*Anal. Chem.*, 1955, **27** [4], 521–525).—Experiments show that in order to describe precisely migration rates, migration sequences and separability, the concentration and sorption of the migrating ions must be specified, as both these parameters have an effect on electrical migration through moist paper. The effects of concn. in the electrophoretic separation of radium from its principal radioactive daughters and from barium have been determined.
K. A. PROCTOR

2319. **Inexpensive stain for paper electrophoresis.** L. A. Rideout and R. W. Prichard (*Science*, 1955, **121** [3141], 374).—Light green SF (**I**) is recommended in place of the relatively expensive bromophenol blue for staining the serum proteins after separation by paper electrophoresis. The strips are dried in an air oven at 105° C for 30 min. and are immersed in 1 per cent. acetic acid for 5 to 8 min. to fix the proteins and minimise loss on developing. They are then stained in 1 per cent. **I** in 1 per cent. acetic acid for 5 to 8 min., washed four times in 1 per cent. acetic acid and air-dried. This method, which also avoids use of $HgCl_2$ and washing with methanol, yields patterns comparable with those given by bromophenol blue.
H. F. W. KIRKPATRICK

2320. **The application of atomic absorption spectra to chemical analysis.** A. Walsh (*Spectrochim. Acta*, 1955, **7** [2], 108–117).—The major obstacle to further progress in spectrochemical analysis is the inter-element effect which, if eliminated, would allow the use of the same set of standards to determine any one element in any material. Atomic absorption spectra appear to have important advantages over emission spectra in being much less susceptible to this effect, particularly from the aspect of absolute analysis. The author examines the theoretical factors governing the relationship between atomic absorption and atomic concentration, and discusses the experimental problems involved in recording such spectra. Experimentally, the measurement of the absorption coefficient consists in measuring the ratio of two intensities, which is much simpler than the measurement of emission intensities in absolute units. The method may offer the possibility of a simple method of isotopic analysis. (30 references.)
K. A. PROCTOR

2321. **Vacuum ultra-violet spectroscopy. A review.** E. C. Y. Inn (*Spectrochim. Acta*, 1955, **7** [2], 65–87).—A review of experimental methods and techniques is presented, with emphasis on recent developments in grating monochromators, background light sources and photomultiplier detectors. Techniques for quant. absorption spectrophotometry and for the measurement of ionisation potentials and photo-ionisation cross-section of molecules are given. Possible applications to problems of molecular structure, the solid state and the upper atmosphere are indicated. (86 references.) K. A. PROCTOR

2322. **Simplifications applicable to the spectrophotometric analysis of a two-component mixture.** J.-M. Bonnier and G. de Gaudemaris (*Bull. Soc. Chim. France*, 1955, **4**, 567–569).—The constituents of a two-component mixture can be determined spectrophotometrically by the solution of two simultaneous equations. When the absorption spectra of the two components are similar and have an isosbestic point, the necessary calculations can be reduced to a simple graphical method. A gain in time is claimed, and a specific example of a mixture of cinnamyl alcohol and cinnamaldehyde is shown to have an error of about 0·6 per cent.
K. A. PROCTOR

2323. **Allowance for impurities of the base metal in synthetic standards for spectrographic analysis.** L. N. Filimonov (*Zavod. Lab.*, 1955, **21** [4], 451–458).—A method of correcting the composition figures for synthetic spectrographic standards for the impurities in the base is described.
G. S. SMITH

2324. **Internal standards in fluorescent X-ray spectroscopy.** I. Adler and J. M. Axelrod (*Spectrochim. Acta*, 1955, **7** [2], 91–99).—Internal standards are of great value in the analysis of ores and minerals of widely varying matrix by fluorescent X-ray spectroscopy, but are subject to disturbing effects, as described by G. von Hevesey ("Chemical Analysis by X-rays and its Applications," McGraw-Hill Book Co., 1932) and R. Glocker and H. Schreiber (*Ann. Physik*, 1928, **85**, 1089). Modern spectrographs afford high speed rather than high resolution so that many of von Hevesey's line pairs are not resolvable. The authors have systematically examined element pairs which are neighbours in the periodic table and which provide resolvable line pairs. Their instrumentation is as previously described (*J. Opt. Soc. Amer.*, 1953, **43**, 769) and briquetted samples of finely divided aluminium powder mixed in a 1:1 ratio were used. Neighbouring elements were found to serve well as internal standards for each other, and the closer the lines the less the likelihood of interference between them. Particle-size variation may introduce substantial errors and homogeneous samples must therefore be prepared. Grinding with silicon carbide for 30 min. in an automatic mortar grinder is the simplest and most rapid method, and gives analyses accurate to about ± 5 per cent. in the worst examples investigated. K. A. PROCTOR

2325. **Application of high-frequency analysis to ion-exchange resins.** M. Honda (*Japan Analyst*, 1953, **2** [5], 456–460).—The electrochemical nature of sorption bands on an ion-exchange resin was studied with the aid of a high-frequency oscillator consisting of an oscillation circuit, which can be shifted vertically along a resin column, and of an automatic recording micro-ammeter. The relationship between the current of the high-frequency circuit and the concn. of an electrolytic soln., in which the resin is kept at an equilibrium state, was closely examined and the mechanism of the change of reactance is discussed. Cations sorbed by a cation-exchange resin have mobilities which are comparable with those in an aq. soln. of concn. 0·1 *N*. K. SAITO

2326. **Experiments on the use of polarography for continuous recording.** Z. Večeřa and V. Zeman (*Chem. Průmysl*, 1954, **4** [2], 60–62; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 46,856).—A polarographic method is used to control the water content

of the reaction mixture in the rearrangement of *cyclo*hexanone oxime to ε-caprolactam; the presence of water retards the rearrangement and promotes hydrolysis of the lactam to ε-aminocaproic acid. The method is based on the difference between the potentials for the separation of H^+ in an anhydrous medium (0·2 to 0·4 V in the presence of SO_3) and in the presence of water (1·2 V). By recording the graph of the current strength against time, the water content of the reaction mixture can be checked and the required amount of fuming sulphuric acid can be added. The polarography is carried out in a special cell at 70° C and the dropping-mercury electrode is replaced by a platinum micro-electrode. E. HAYES

2327. **Selection of the "zero line" in polarography.** N. Z. Bruja (*Rev. Chim.*, 1953, **4** [2], 30–36; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 46,795).—When the element being determined polarographically gives an incomplete wave (the branch due to the residual current being absent), the height of the wave is measured not from the zero line of the galvanometer but from the upper branch of the diffusion-current wave obtained by polarographing the supporting electrolyte. The method eliminates the necessity of preparing a standard for each separate analysis and increases the precision of the determination. E. HAYES

2328. **Effect of adsorption on the anodic polarographic wave; formation of non-turbulent maxima and minima.** P. Zuman (*Chem. Listy*, 1954, **48** [7], 1025–1030).—In the presence of phosphates or of barbitone, the anodic wave of oxidisable substances is subject to deformations, caused by the formation of an adsorbed film at a sufficiently positive potential. Similar changes observed in solutions of thiobarbiturates and other thio compounds are due to the formation of adsorbed layers at potentials more positive than the potential at which a diffusion-controlled anodic wave is formed, corresponding to salt formation with mercury. The adsorption currents give rise to non-turbulent maxima and minima on the polarographic curves. G. GLASER

2329. **Voltammetry at constant current. Review of theoretical principles.** P. Delahay and G. Mamantov (*Anal. Chem.*, 1955, **27** [4], 478–483).—This paper reviews the principles of the method of electrolysis known as chronopotentiometry. It is considered to have possible advantages over other electrochemical techniques (particularly conventional polarography) in possessing (*a*) good precision, (*b*) no fluctation in the measured quantity, as opposed to the fluctuations in the diffusion current in polarography, (*c*) the possibility of determining concn. as low as 10^{-6} *M*, (*d*) the possibility of using solid or mercury electrodes, (*e*) the possibility of use in two-component systems without separation. On the other hand, no steady reading is observed and the consumption of mercury is greater than in polarography. (27 references.)
K. A. PROCTOR

2330. **Voltammetry at constant current. Experimental evaluation.** C. N. Reilley, G. W. Everett and R. H. Johns (*Anal. Chem.*, 1955, **27** [4], 483–491).—The applications of chronopotentiometry to the cathodic reduction and anodic oxidation of single and mixed ions in solutions of concn. 5×10^{-5} to 1×10^{-2} *M* by platinum and mercury-pool electrodes are described. Transition times vary between 4 and 60 sec. Two runs only per solution can be made with reproducible results. Several supporting electrolytes are examined and details of practical apparatus and technique are given.
K. A. PROCTOR

2331. **Studies on controlled potential electrolysis. I–III. Its applications to electro-gravimetric and polarographic analyses and their instrumentations.** M. Ishibashi and T. Fujinaga (*Japan Analyst*, 1953, **2** [4], 342–347).—The electrolytic deposition of copper and bismuth was studied in weakly acid soln. containing tartrate. By the use of an automatic voltage regulator designed by the authors, the cathodic potential could be kept constant with an accuracy of ± 10 mV. Results are given on the relation between the composition of the electrolytic soln. and the deposition potential. Copper (< 0·5 g) is deposited free from Sb and Bi on the cathode from a weakly acidic soln. (pH 5·8) containing tartrate, succinate and hydrazine at − 0·30 ± 0·01 V *vs.* the S.C.E. Bismuth (< 0·3 g) is deposited subsequently from the same soln. at − 0·40 V *vs.* the S.C.E. The efficiency of the separation of Bi and Pb from Cu and from each other was investigated by the use of Th-C and Th-B, obtained from natural radiothorium, as indicators. Pb, Cd and Zn are determined polarographically in the residual electrolytic soln. after the addition of ammonium acetate and tartaric acid as supporting electrolytes. This method can be applied to the analysis of copper metal and alloys. K. SAITO

2.—INORGANIC ANALYSIS

2332. **Continuous analysis of ortho- and para-hydrogen mixtures.** D. H. Weitzel and L. E. White (*Rev. Sci. Instrum.*, 1955, **26** [3], 290–292).—The adaptation of a commercial thermal conductivity unit for continuous analysis of mixtures of ortho- and para-hydrogen is described.
G. SKIRROW

2333. **Chromatographic semi-micro analysis of gases. X. Determination of small and trace amounts of helium, neon and hydrogen in gases.** J. Janák and K. Tesařík (*Chem. Listy*, 1954, **48** [7], 1051–1057).—A method for the determination of He and Ne in natural gas in concentrations from 10^{-3} to 10^{-4} vol. per cent. is described. In a special apparatus (illustrated) a known volume of the gas is concentrated by adsorption on activated carbon at the temp. of liquid air (− 185° C). The non-adsorbable concentrate is isolated by means of the Töpler pump, freed from H by combustion over CuO, and analysed by chromatography. By working at − 78° to − 100° C, H present in other gases in concentrations from 10^{-1} to 10^{-3} vol. per cent. can also be determined. The method which, unlike older methods, eliminates the necessity of previously removing hydrocarbons and absorption of residual N by calcium metal, is illustrated by the determinations of He and Ne in natural gas and in air, and of H in argon, in electrolytic oxygen and in nitrogen used for electric bulbs. G. GLASER

2334. **Improvements in Karl Fischer method for determination of water.** E. D. Peters and J. L. Jungnickel (*Anal. Chem.*, 1955, **27** [3], 450–453).—The use of 2-methoxyethanol as a solvent instead of methanol in the Karl Fischer method for determination of water is investigated. The modified reagent is claimed to be more versatile and stable in the direct and dead-stop end-point procedures. For the determination of water in ketones and

some aldehydes, a glycol - pyridine (4 + 1) mixture is recommended as solvent. D. A. PANTONY

2335. **Determination of water vapour with an infra-red analyser.** K. F. Luft and R. Guérin (*Chim. Anal.*, 1955, **37** [3], 100–103).—The use of the infra-red analyser previously described (*Z. tech. Phys.*, 1943, **24** [5], 97) permits the determination of 0 to 2 per cent. of water vapour, with a precision of ± 2 per cent., in N, O, H, CO, air and other gases having little absorption in the region 5·5 to 7·5 μ. Because of difficulties associated with condensation, NH_3 is used instead of water vapour for measuring the amount of radiation absorbed; the i.r. spectra of H_2O and NH_3 overlap considerably at the wavelengths used. The method is rapid and requires only a small volume of sample. A. R. ROGERS

2336. **Rapid determination of water in silicate rocks.** L. Shapiro and W. W. Brannock (*Anal. Chem.*, 1955, **27** [4], 560–562).—The Penfield procedure for determining total water in silicate rocks is modified to reduce the time required to < 10 min. per sample. The water is expelled from the sample in a test-tube, and is absorbed on a pre-weighed strip of filter-paper placed inside the tube. The paper is subsequently reweighed, and the water content of the sample is calculated from the change in wt. of the paper and a handling correction. The same degree of accuracy as the Penfield method is claimed. D. R. GLASSON

2337. **Separation and identification of alkali metals by paper chromatography.** T. Barnabas, M. G. Badve and J. Barnabas (*Naturwissenschaften*, 1954, **41** [20], 478).—Pentanol - methanol (3:7) and ethanol - methanol (1:1) are good solvent mixtures for the separation of the alkali metals; lithium, ammonia, sodium and potassium (as chlorides) migrate in this order. The metals are revealed by a spray consisting of indophenol dye and silver nitrate (0·2 g of 2:6-dichlorophenol-indophenol dissolved in 100 ml of ethanol to which 3 g of $AgNO_3$ are added, and filtered). The chlorides appear pink against a blue background, and on exposure to air turn dark brown against a light-brown background. E. KAWERAU

2338. **A volumetric determination of sodium chloride in crude sea salt.** S. Shinkai (*Japan Analyst*, 1953, **2** [5], 442–443).—When NaCl is treated with HF in the presence of H_2SiF_6, Na_2SiF_6, equivalent in amount to the NaCl, is obtained. After the removal of HCl and excess of HF and H_2SiF_6 by heating, Na_2SiF_6 is titrated with 0·5 *N* NaOH soln. Potassium chloride reacts in a similar way, and the amount should be determined and subtracted from the result. *Procedure*—The sample (1 g) is treated with 0·5 *N* H_2SiF_6 (≃ 50 ml) and HF (40 per cent.) (10 ml) in a platinum or silver dish and heated to dryness until there is no smell of acid. The residue is dissolved in water (100 ml) and titrated with 0·5 *N* NaOH, with phenolphthalein as indicator. The amount of K is determined by the usual cobaltinitrite method and subtracted from the result. K. SAITO

2339. **The quantitative determination of potassium as the tetraphenylboron salt.** K. Sporek and A. F. Williams (*Analyst*, 1955, **80**, 347–354).—A critical examination of published procedures for the determination of K as the tetraphenylboron salt showed that to obtain a ppt. readily separable by filtration the final acidity of the reaction mixture should be > 0·2 *N*, and that to prevent decomposition of the reagent the temp. should be maintained at 0° C. *Procedure*—The aq. soln. containing ≃ 20 mg of K is treated with 2 ml of conc. HCl, the vol. is adjusted to 50 ml and the liquid is cooled in ice - water for ≃ 10 min. A cooled soln. (25 ml) of a 1 per cent. (v/v) soln. of sodium tetraphenylboron in 0·01 *N* NaOH is added and the mixture is maintained at 0° C for 10 min. The ppt. is collected in a sintered-glass crucible (porosity No. 4) or in a Gooch crucible with a thin asbestos pad, and is washed with three 10-ml portions of water freshly saturated with potassium tetraphenylboron and which need not be cooled. The ppt. is dried for 1 hr. at 110° to 120° C. 1 g ≡ 0·10912 g of K. Of the commonly occurring ions only Ce^{++++}, Cu^{+}, Hg^{++}, Ag and Th are precipitated by the reagent. Some organic bases (*e.g.*, diphenylamine, pyridine, quinaldine and quinoline) give precipitates. Potassium in 20-mg amounts can be accurately determined in the presence of about 100 times as much Na, but above this ratio high results are obtained. Ammonium ions are known to react in the same way as K. A. O. JONES

2340. **The determination of potassium by precipitation as potassium tetraphenylboron and its application to silicate analysis.** H. J. Cluley (*Analyst*, 1955, **80**, 354–364).—From an examination of methods advocated for the pptn. of potassium tetraphenylboron, two methods involving pptn. at pH 2 and pH 6·5, respectively, have been developed. *Procedure*—In the pH 2 method the KCl soln. (1 to 24 mg in 80 ml) is treated with 10 ml of 0·1 *N* HCl and then with 8 ml of a 3·4 per cent. (w/v) soln. of sodium tetraphenylboron added in drops from a burette during 3 min. with constant stirring. After 30 min. the ppt. is collected on a No. 4 sintered-glass crucible, washed with 2 to 3-ml portions of a saturated soln. of potassium tetraphenylboron and then once with 1 or 2 ml of water. The ppt. is dried at 120° C. In the pH 6·5 method the KCl soln. (90 ml) is treated with 3 drops of 0·1 *N* acetic acid and 3 drops of bromocresol purple indicator and then with 0·1 *N* NaOH until the indicator just becomes distinctly purple. The procedure is then as in the pH 2 method. In the presence of other elements the pH 2 method may be applied as described, but in the pH 6·5 method 1 g of EDTA (disodium salt) (**I**) is added. No appreciable error is obtained in the presence of substantial amounts of Mg, Ca, Ba, Zn, Pb, Al and Fe, and lesser amounts of Cr, Cu, Co, Mn, Ni, Ti, As and Sb. To apply these methods to glass analysis the sample is decomposed with HF and $HClO_4$, the mixture is evaporated to dryness and the residue is dissolved in either 10 ml of 0·1 *N* HCl or in 20 ml of a 5 per cent. soln. of **I**, according to the method to be used. For refractories the finely ground sample (0·5 g) is decomposed by the Lawrence Smith process in the usual manner, care being taken that the final residue is free from ammonium salts. The residue is boiled with water (60 ml) for 30 min., thus reducing the vol. to 40 ml. The soln. is filtered through Whatman No. 40 paper and the residue is washed 10 times with hot water. The filtrate is cooled and its vol. is adjusted to 100 ml. A 50-ml aliquot is treated either (*a*), with *N* HCl in drops until the soln. is just acid to litmus, and then with 1 ml in excess, and is diluted to 90 ml, or (*b*), with 20 ml of a 5 per cent. soln. of **I**, 3 drops of bromocresol purple indicator and *N* NaOH until the indicator just shows a distinct purple colour,

and is then diluted to 90 ml. The procedure is then as already described. Blank determinations should be made with known amounts of K which are deducted to ascertain the reagent blank.

A. O. JONES

2341. **Determination of potassium.** F. L. Hahn (*Z. anal. Chem.*, 1955, **145** [2], 97–98).—The tetraphenylborate ion can be directly titrated with $AgNO_3$, with K_2CrO_4 as indicator, in aqueous acetone solution. This reaction can be used as the basis of a method for the determination of K.

A. J. MEE

2342. **Quantitative determination of potassium with sodium cobaltinitrite by various modifications and the effect of some ions on the analytical result.** R. V. Kotlyarov (*Izv. Timiryazevskoĭ S.-Kh. Akad.*, 1954, [1], 189–196; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 50,199).—One gravimetric and five volumetric modifications of the cobaltinitrite method for the determination of K are compared, and the effects of other cations and anions are studied. Titration with a soln. of the reagent, added drop by drop with constant stirring, gives the best results. The determination is not affected by Mg^{++}, Ca^{++}, Mn^{++} or SO_4'', or by small amounts of Na^+, Sr^{++}, Zn^{++} or Cu^{++}. Large amounts of the latter group, or Ba in any amount, interfere. Precipitation with $NaPb[Co(NO_2)_6]$ (Sergeenko's method) is unsatisfactory, since the composition of the ppt. does not correspond to $KPb[Co(NO_2)_6]$.

E. HAYES

2343. **Rapid determination of copper in aluminium metal and alloys.** O. Kammori and K. Mukaewaki (*Japan Analyst*, 1953, **2** [4], 313–316).—The unfavourable influence of iron on the iodimetric determination of Cu in Al alloys can be eliminated by adding NH_4F to the soln. to be titrated. Thus a rapid (< 15 min.) determination of Cu (0·1 to 15 per cent.) is provided. The deviation of the results from those obtained by the standard method is ± 0·02 per cent. *Procedure*—The sample (0·5 g) is decomposed with 20 per cent. NaOH soln. (≃ 15 ml), diluted to 100 ml and filtered (without washing). The residue is dissolved in warm dil. HNO_3 (1 + 1) (10 ml) and neutralised with aq. NH_3 soln. (sp. gr. 0·88, 1 + 1). Acetic acid (30 per cent., 5 ml) and $NaNO_2$ soln. (3 per cent., 3 to 4 drops) are added (to decompose higher oxides of Mn). The mixture is boiled with urea (1 g), cooled, treated with NH_4F (1 g) and KI (5 g, or 1·5 g of KI and 2 g of KSCN) and titrated with 0·02 *N* $Na_2S_2O_3$ soln. K. SAITO

2344. **An improvement in the iodide method for copper, with fluoride as inhibitor of iron.** R. B. Martin (*Analyst*, 1955, **80**, 318).—In the determination of Cu by addition of KI and titration with standard $Na_2S_2O_3$ the pH of the soln. is adjusted to 3·5 to 4·0 before addition of NH_4HF_2 to inhibit Fe. This pH range is critical and is usually secured by addition of aq. NH_3 until a faint odour of NH_3 is perceptible (Vogel, "A Textbook of Quantitative Inorganic Analysis," 2nd Ed., Longmans, Green & Co., London, 1951, p. 344). It is now suggested that addition of a few drops of methyl orange indicator before addition of aq. NH_3 gives a more convenient indication of the desired condition, since a sharp colour change from purple to green occurs when enough aq. NH_3 has been added. The subsequent addition of NH_4HF_2 should restore the purple colour. The colour change at the end-point of the titration from the blue of the starch-iodide to pink is as sharp as when methyl orange is not used. A. O. JONES

2345. **Tetraethylthiuram disulphide as an analytical reagent. II. Photometric determination of copper.** J. Michal and J. Zýka (*Chem. Listy*, 1954, **48** [7], 1043–1046).—The basis of the present method for the photometric determination of Cu in the presence of other metals is the formation of an intense yellow-brown coloration, with an absorption max. at 445 mμ, when Cu reacts with tetraethylthiuram disulphide (**I**). In the presence of Hg^{++} an excess of the reagent should be used, for Hg^{++} also forms a stable, though colourless, complex with **I**. Coloured cations, if present in high concn., may interfere. The following procedure is recommended for the determination of Cu in the presence of an excess of Fe. Remove all Fe by two precipitations in the hot with aq. NH_3 and filtering, dilute the combined filtrates with water to 100 ml, acidify a 25-ml aliquot with HCl, treat the soln. with 96 per cent. ethanol (20 ml) and a 0·01 *M* ethanolic soln. of **I** (3 ml), dilute with ethanol to 50 ml and measure the extinction after 20 min.

G. GLASER

2346. **Extraction of metal thiocyanate complexes with tributyl phosphate. Copper (II) thiocyanate.** L. M. Melnick and H. Frieser (*Anal. Chem.*, 1955, **27** [3], 462–463).—The extraction of $Cu(SCN)_2$ into tributyl phosphate from aq. media at various pH levels, temp. and Cu^{++} to SCN' ratios is examined. In general, quant. extraction is achieved with pH values > 2·5, temp. < 20° C and a SCN' to Cu^{++} ratio of 24 to 1. The org. extract exhibits an absorption max. at 382·5 mμ (extinction coeff., 620). D. A. PANTONY

2347. **A simple method of amperometric titration of copper sulphate with sodium carbonate solution using copper electrodes.** J. Kamecki and L. Suski (*Roczn. Chem.*, 1955, **29** [1], 115–117).—A method simpler than that of the dropping-mercury or rotating platinum electrode was used for titrating 0·02 *N* $CuSO_4$ soln. with 0·25 *N* Na_2CO_3 soln. The electrodes are two copper wires immersed in the stirred suphate soln. The equivalence point can be deduced satisfactorily from the graph of the current in the circuit (a diagram of which is given) against the volume of the carbonate soln. added.

A. O. JAKUBOVIC

2348. **Polarographic determination of copper and iron.** J. Doležal and P. Hofmann (*Coll. Czech. Chem. Commun.*, 1955, **20** [1], 147–150).—In a soln. of ethylenediamine tartrate (**I**) (0·5 *M*) and $K_4P_2O_7$ (**II**) (0·1 *M*), Cu^{II} gives a well-defined diffusion wave with $E_{\frac{1}{2}} = -0{\cdot}25$ V (*vs.* the S.C.E.). For a constant concn. of **I**, an increase in the concn. of **II** or in the pH of the electrolyte makes the half-wave potential more negative, but the form of the wave is unchanged. In the same electrolyte Fe^{III} also gives a well-defined wave with $E_{\frac{1}{2}} = -0{\cdot}43$ V, and with increasing pH this value becomes more negative; with higher concn. of **II**, the form of the wave is changed. The two metals can be determined together if the Cu:Fe ratio is between 15:1 and 1:20; higher proportions of Cu distort the Fe wave. Mn, Ni, Co, Zn, As, Sb, Cd, Ti, Mo, U, Ce, Se, Te, W, Cr and V do not interfere. High concentrations of Pb ($E_{\frac{1}{2}} = -0{\cdot}58$ V) affect the determination of Fe. Fe cannot be determined in the presence of Bi, which is reduced at a more positive potential ($E_{\frac{1}{2}} = -0{\cdot}40$ V). Neither Pb nor Bi affects the determination of Cu. (This is a translation into Russian of a paper previously published in *Chem. Listy*, 1954, **48**, 1325.) E. HAYES

2349. **New organic reagent for silver and copper.** B. Gehauf and J. Goldenson (*Anal. Chem.*, 1955, **27** [3], 420–421).—A compound, named Zolon red, prepared by the action of chloramine T on a mixture of NaCN, pyridine and 3-methyl-1-phenyl-5-pyrazolone in boiling aq. soln. (preparation described), is examined as a reagent for the detection of $Ag^{\cdot}$ and $Cu^{\cdot}$. Deep-blue insoluble compounds are produced with $Ag^{\cdot}$ and $Cu^{\cdot}$ alone; Au^{III} gives a purple flocculent ppt., and $Hg^{\cdot\cdot}$ a similar red ppt. $Pb^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, Pt^{IV} and Pd^{II} do not react. Limits of sensitivity are: $Ag^{\cdot}$, 1 in 6×10^5, and $Cu^{\cdot}$, 1 in $2{\cdot}5 \times 10^5$. The reagent can be used as an external indicator in titrations of $Ag^{\cdot}$ with Cl'. D. A. PANTONY

2350. **Quantitative spectrometric analysis of silver in intermediate products and industrial wastes.** V. P. Sȳchev (*Tr. Sib. Fiz.-Tekhn. In-ta*, 1953, [32], 67–73; *Referativnȳĭ Zh., Khim.*, 1954, Abstr. No. 43,474).—Silver, in amounts of 10^{-4} to 10^{-2} per cent., is determined by means of the spectrograph ISP-22 with a d.c. carbon arc. The continuous spectral background homologous to the Ag lines 3383 and 3281 is used as an internal standard. E. HAYES

2351. **Complex citrates of metals in inorganic analysis. II. Separation and estimation of silver and lead in a mixture.** A. K. Mukherji and A. K. Dey (*Z. anal. Chem.*, 1955, **145** [2], 93–96).—An excess of Na citrate is added to the mixture containing Ag and Pb. The insol. citrates of Ag and Pb, which are at first precipitated, re-dissolve as complex citrates. If HCl is added to the solution only AgCl is pptd., and it may be estimated gravimetrically. Pb may be determined in the filtrate as lead chromate. A. J. MEE

2352. **Quantitative analysis without separation. XII. Gravimetric analysis without separation for the systems Ag - Hg and Pb - Hg.** N. Unohara (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [11], 1183–1185).—The thermal decomposition curves of chromates of Ag, Hg, Pb and their binary mixtures were examined with a thermobalance. The determination of Hg by use of the weight decrease on heating the chromate with those of Ag or Pb provides reasonable results when the amount of Hg is greater than that of Ag or Pb. K. SAITO

2353. **Chemical analysis of beryllium. IV. Determination of beryllium by the use of ammonia in the presence of borax.** Tomayaki Akiyama (*Japan Analyst*, 1953, **2** [4], 354–355).—Experimental conditions for the pptn. of Be by the addition of aq. NH_3 soln. in the presence of NH_4Cl and BO_3''' were studied. Beryllium hydroxide is precipitated through decomposition of the compound $Be(BO_2)_2(HBO_2)_2$ at pH 5·85 to 6·75. The precipitate is apt to adsorb BO_3''' and requires a thorough washing. Interference results from the presence of $Al^{\cdot\cdot\cdot}$ and ions of alkaline-earth metals. **V. Determination of beryllium by the use of caustic alkali.** (*Ibid.*, 1953, **2** [4], 355–358).—The solubility of BeO in caustic alkali soln. of different concn. was measured and its application to the separation of Be from Al, Fe, Ca and Mg was studied. $Be(OH)_2$ is precipitated free from Al by keeping a basic soln. (pH $\simeq$ 9·4, NaOH $\simeq$ 0·5 *N*) of sodium beryllate and aluminate on a boiling-water bath for 40 min. Ferric iron should be removed from an HCl soln. by shaking with ether. Ca and Mg are retained in soln. when Fe, Al and Be are precipitated by the addition of NH_4NO_2 and methanol. **VI. Determination of beryllium with sodium bicarbonate.** (*Ibid.*, 1953, **2** [4], 358–359).—The attempt to separate Be from Al and Fe by precipitating $Fe(OH)_3$ and $Al(OH)_3$ with $NaHCO_3$ met with little success despite careful control of experimental conditions. $Be(OH)_2$ obtained from the filtrate by the addition of aq. NH_3 soln. is contaminated with $Al(OH)_3$, which, for an accurate determination of Be, must be subsequently removed by the oxine method. **VII. Determination of beryllium with tannin.** (*Ibid.*, 1953, **2** [5], 460–462).—The separation of Be from Al, $Fe^{\cdot\cdot\cdot}$, MoO_4'', VO_4''' and Ti with tannin was studied. Be is separated from Al satisfactorily by re-pptn. Fe should be removed with H_2S before the addition of tannin. Mo and V can be precipitated free from Be in an acetic acid soln. with tannin, and Be is determined in the filtrate. Ti is precipitated similarly in an oxalic acid soln., but the Be - tannin ppt. which is obtained from the filtrate is contaminated with Ti. **VIII. Separation of beryllium with ammonium sulphide.** (*Ibid.*, 1953, **2** [5], 462–463).—Experimental conditions for the separation of Be from Fe^{III}, Co, Ni and Mn were examined. The first three are pptd. with $(NH_4)_2S$ in an ammoniacal soln. containing tartrate. Manganese is removed by pptn. with $KClO_3$ and H_2O_2 in HNO_3 soln. Beryllium is determined in the filtrate by either the tannin method or the phosphate method. Al should be removed with oxine. **IX. Separation of beryllium with hydrogen sulphide.** (*Ibid.*, 1953, **2** [5], 463–464).—A similar experiment was carried out by the use of H_2S in aq. NaOH soln. Pptn. of Mn as sulphide is not satisfactory, since MnS adsorbs a significant amount of Be. K. SAITO

2354. **Titration of magnesium in presence of aluminium.** J. A. Ritchie (*Analyst*, 1955, **80**, 402).—In the presence of Al, Mg can be titrated with EDTA if triethanolamine is used as a masking agent (Přibil, *Coll. Czech. Chem. Commun.*, 1954, **19**, 465). The blue end-point is transient, rapidly changing back to purple, and may cause uncertainty. If the test soln. is first cooled to below 5° C, the end-point is sharp and stable, even with dil. solutions on a semi-micro scale. A. O. JONES

2355. **The determination of trace elements in magnesium and its alloys by spectrographic procedures.** W. J. Price (*Spectrochim. Acta*, 1955, **7** [2], 118–127).—The detection and determination of about 20 elements at trace concentrations are reported. The methods employed are: (*i*) with solid samples and interrupted arc or high-voltage spark excitation, (*ii*) with sample in solution and high-voltage spark excitation. A medium spectrograph can be used if rare earths and Th are absent. The normally encountered concn. of Zr (< 1 per cent.) has a negligible effect on the determination of other elements, but the effect of Al is such that in high concn. (1 to 10 per cent.) special standards must be provided. The effect of Zn at concn. < 3 per cent. can be ignored unless very high accuracy is required. Line pairs and sensitivities are quoted for all elements concerned. In the range 0·01 to 0·1 per cent. a coefficient of variation of about 6 to 8 per cent. is to be expected. The interrupted arc yields reproducibilities as good as those obtained by the spark method. K. A. PROCTOR

2356. **Complexes of Eriochrome black T with calcium and magnesium.** A. Young and T. R. Sweet (*Anal. Chem.*, 1955, **27** [3], 418–420).—Examination of the light-absorption curves of various mixtures of Ca^{++} or Mg^{++} with aq. Eriochrome black T at different pH levels by the method of continuous variations shows that Mg^{++} forms a 1:1 complex at pH 8·41, a 1:2 complex at pH 9·52 and 1:3 at 11·70. The values for Ca^{++} are: 1:2 at pH 10·61 and 1:3 at pH 12·4. Mixtures of complexes are formed at intermediate pH values.
D. A. PANTONY

2357. **Simultaneous spectrophotometric determination of calcium and magnesium.** A. Young, T. R. Sweet and B. B. Baker (*Anal. Chem.*, 1955, **27** [3], 356–359).—A soln. (50 ml) containing 0·3 to 6 p.p.m. of Ca^{++} and of Mg^{++} is treated with buffered Eriochrome black T soln. (25 ml) and a piperidine - HCl buffer soln. (pH 11·7) (5 ml) or aq. NH_3 - HCl (pH 9·52) soln. The soln. is made up to 100 ml with water and stored in the dark for 60 min., when the absorption is measured at 630 mμ with respect to a reagent blank. By means of a given equation, the decrease of absorption due to Ca^{++} and Mg^{++} at pH 11·7 and 9·52 is converted to the concn. of the alkali metals. The error is given as 0·12 p.p.m. of Ca^{++} and 0·09 p.p.m. of Mg^{++}. The interferences of Na^{+} and K^{+} are discussed. D. A. PANTONY

2358. **Separation of barium and strontium by chromatography on cellulose. I. Chromatography on paper strips.** J. Fouarge (*Anal. Chim. Acta*, 1955, **12** [3], 231–238).—The chromatographic separation on paper of Ba^{++} and Sr^{++} has been investigated with the use of radio-isotopes of the metals. Mixtures of methanol with various other liquids are used as eluting solvents, and the best separation is obtained with a mixture of methanol and 12 *N* HCl (20 + 1, by vol.); for this solvent, R_F (Ba) = 0·1, R_F (Sr) = 0·3. The bands are developed with rhodizonate and measured with a Geiger - Müller counter. **II. Chromatography on cellulose powder.** (*Ibid.*, 1955, **12** [4], 342–350).—The chromatographic behaviour of Ba^{++} and Sr^{++} on a cellulose-powder column has beeni nvestigated with the aid of radioactive isotopes ^{140}Ba and ^{90}Sr. Satisfactory separations of the two metals are obtained with the use of 1·2 *N* HCl in methanol to which is added 3 to 5 per cent. of water, and with a methanol - ether (3 + 1, by vol.) mixture to which is added 2 to 5 per cent. of 12 *N* HCl. The latter mixture, with 5 per cent. of 12 *N* HCl, is effective with as little as 0·001 μg of Sr^{++} and 1 μg of Ba^{++}; it also enables ^{140}Ba and ^{90}Sr to be separated from their respective decay products ^{140}La and ^{90}Y.
W. C. JOHNSON

2359. **Spot-test method for the detection of cadmium in presence of copper, lead and tin.** M. R. Verma and S. D. Paul (*Analyst*, 1955, **80**, 399–401).—A spot-test method for the detection of Cd in the presence of large amounts of Cu, Pb and Sn has been developed. *Procedure*—One drop (0·05 ml) of the test soln. is allowed to dry on the centre of a circle of filter-paper (Whatman No. 1 or 4). Dilute aq. NH_3 (1 + 1) is then added in similar drops so that the liquid front travels to ≃ 3 cm from the centre. The paper is dried in hot air and the alternate addition of aq. NH_3 and drying is repeated two or three times, further movement of the periphery of the liquid front being avoided. This effects clean separation of the ions into two main groups, *viz*, Cu and Cd as complex ammonium salts at the periphery and Pb and Sn as hydroxides at the centre. The paper while still wet (with the last flooding) is then exposed to H_2S for 1 or 2 min., when all four ions are fixed as sulphides. The dried paper is irrigated with 10 per cent. w/v aq. KCN soln., when the Cu complex moves still further out leaving the yellow cadmium ring between the black lead and tin sulphides at the centre and the almost colourless rim of complexed Cu. The test may be applied to the detection of Cd in copper-based alloys by placing a drop of the appropriate acid on the alloy surface and, after attack has proceeded for 1 or 2 min., transferring it to filter-paper and proceeding as described. A. O. JONES

2360. **Compleximetric titration of aluminium.** E. Wänninen and A. Ringbom (*Anal. Chim. Acta*, 1955, **12** [4], 308–318).—Aluminium is determined in a soln. by adding an excess of ethylenediaminetetra-acetic acid (EDTA) and titrating the excess with a standard soln. of Zn^{++}, dithizone being used as indicator. The following conditions are derived from a theoretical treatment (*cf. Anal. Abstr.*, 1954, **1**, 2616) and yield satisfactory results in practice. *Procedure*—To the sample soln. containing 0·2 to 0·5 millimole of Al^{+++} add a standard soln. containing 0·3 to 0·7 millimole of the disodium salt of EDTA. Add 10 ml of buffer soln, pH 4·5 (*M* acetic acid - *M* NH_4 acetate) and ethanol to produce a concn. of 40 to 50 per cent. by vol. Add 2 ml of a fresh 0·025 per cent. w/v ethanolic soln. of dithizone and titrate with 0·05 *M* $ZnSO_4$ to a colour change from greenish-violet to red.
W. C. JOHNSON

2361. **Complex colorimetric determination of aluminium.** D. Eckardt, L. Hartinger and L. Holleck (*Angew. Chem.*, 1955, **67** [6], 178).—Small quantities of Al (0·5 to 3·5 × 10^{-4} *M*) can be determined by measurement of the red colour of the complex with aurinetricarboxylic acid, if the pptn. of the lake is prevented by addition of sulphosalicylic acid at concn. of 1·0 × 10^{-3} *M*. A linear relation exists between wt. of Al and the extinction coeff. of the colour of the Al - aurinetricarboxylic acid - sulphosalicylic acid complex if the pH is kept at 8 with borate buffer. The effects of concn. of reagents on the extinction coeff. are described. S.C.I. ABSTR.

2362. **Studies on aluminium in steel. I. The quantitative separation of aluminium and its compounds.** K. Narita (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [10], 1037–1041).—The determination of Al in metallic, nitride and oxide forms in steel was studied, with special reference to the nitride. Aluminium oxide and silicates are stable toward treatment with Br and ethyl acetate. Aluminium nitride in steel behaves in the same way as synthesised aluminium nitride and is also stable toward treatment with Br and ethyl acetate; it is, however, soluble in 5 per cent. NaOH soln. to give NH_3 and sodium aluminate, whereas Al_2O_3 remains unchanged. Total Al is determined colorimetrically with aluminon at pH 5·3 after the removal of Fe by electrolysis using a mercury cathode. For the determination of Al in the form of nitride and oxide, the sample (2 g) is decomposed by refluxing with Br (8 ml) and ethyl acetate (12 ml), and filtered. The residue is treated with H_2SO_4 and HF, and Al is determined colorimetrically with aluminon. For the determination of AlN, the residue obtained as above is distilled with conc. NaOH soln. The ammonia in the distillate is determined by means of Nessler's reagent. K. SAITO

2363. **The spectrochemical determination of gallium in blende.** D. F. C. Morris and F. M. Brewer (*Spectrochim. Acta*, 1955, **7** [2], 88–90).—In order to confirm radioactive analyses the authors present a spectrochemical procedure with the cathode-layer carbon arc, with Zn as internal standard, on a large Hilger fully automatic, quartz-prism Littrow instrument. Agreement between the two methods is good and the precision of the spectrochemical procedure is such that over a range of 0·005 to 0·02 per cent. of Ga the standard deviation is ± 5 per cent.

Electrodes were prepared from 3-cm lengths of pure carbon rod, 5 mm in diameter, by cutting down to a diameter of 3 mm over a length of 17 mm and boring a recess 4 mm deep and 1/16 in. in diameter. One electrode was filled with the sample and used as cathode, a similar unbored electrode being used as anode.

The optical system involved focusing an image of the arc on a screen with a Hilger F958 lens and passing 2 mm of this image adjoining the cathode through a diaphragm and on through a Hilger F1025 lens at the slit, giving a focus at the collimator. The arc was made by bringing the electrodes together and allowing the current to flow for a few sec. at 3 amp., then separating them to 4 mm and increasing the current to 9 amp. Exposures of 40 sec. were given with Ilford rapid panchromatic plates developed for 3 min. in Ilford ID2 at 18° C.

Intensities of Ga 2943·6 A and Zn 3072·1 A were compared by measuring their transmissions and using a characteristic curve obtained from an iron arc with step sector. Background intensities were subtracted and the ratio of the corrected intensities for a series of standards was plotted against percentage of Ga on log - log co-ordinates to give a working curve.

Since blende has different burning characteristics from pptd. ZnS, dilutions of Specpure Ga_2O_3 with a Ga-free blende were made to give standards containing 0·05, 0·02, 0·01 and 0·005 per cent. of Ga. K. A. PROCTOR

2364. **Isolation and determination of small amounts of indium with sodium diethyldithiocarbamate.** V. Patrovský (*Chem. Listy*, 1954, **48** [7], 1047–1050).—Indium is quantitatively precipitated with Na diethyldithiocarbamate (**I**) in the pH range 7 to 11. Much Sn and Sb interferes; any excess of Zn and Fe should also be removed. *Determination of In in ores containing Zn and Fe*—Decompose the sample (5 to 20 g) with acid or by alkaline fusion, evaporate the mixture with conc. H_2SO_4 (10 to 30 ml) to white fumes, dilute the residue to a 5 to 8 per cent. H_2SO_4 concn., filter off SiO_2 and $PbSO_4$, and add aq. NH_3 to pH 1. Reduce all Fe with the required amount of a saturated soln. of $Na_2S_2O_3$; the soln. becomes decolorised. Boil it to separate the sulphides of Cu, Bi, Sb, Ag and Pb, and adjust the pH to 6 by the addition of a saturated soln. of hexamethylenetetramine; boil the soln., rapidly collect the ppt. (Al, Ga, In and Sn) by suction, wash it with warm water, dissolve it in HCl and bring the soln. to boiling point after adding $KClO_3$. Treat it with 10 per cent. Na K tartrate, make alkaline with NaOH or aq. NH_3, add KCN to hold up Zn, Cu, Cd and other elements, and precipitate In in the warm with a 2 per cent. soln. of **I** (10 to 25 ml). Wash the ppt. on the filter with warm water containing tartrate and then with water alone, and either dry the ppt. at 105° C and weigh it as such (factor 0·2050), or convert it into In_2O_3 by calcining at 900° C (factor 0·8270). If required, the ppt. of In diethyldithiocarbamate can be also quantitatively extracted with chloroform or ethyl acetate. G. GLASER

2365. **Colorimetric method for determining small amounts of thallium.** V. S. Fikhtengol'ts and N. P. Kozlova (*Zavod. Lab.*, 1955, **21** [4], 407–408).—The method is designed for determining small amounts of Tl in the air. Oxidation of Tl^{I} to Tl^{III} is effected best by Cl from the reaction of $KMnO_4$ and HCl. The colorimetric determination is based on the reaction of $TlCl_3$ with KI and the intensity of the colour of the iodine liberated with starch. *Procedure*—A known volume of air is sucked through a tube containing cotton wool moistened with *N* HCl. The cotton wool is extracted by three treatments with boiling *N* HCl and the extract is heated with 2 to 3 ml of 0·1 *N* $KMnO_4$ until the liquid is colourless. The solution is evaporated to dryness, the residue is dissolved in 5 ml of 0·1 *N* HCl and mixed with 1 ml of freshly prepared 0·2 per cent. KI solution and 1·5 ml of starch solution, prepared by mixing 0·5 g of starch with 20 ml of 13 per cent. NaCl solution, adding the mixture to 80 ml of boiling 13 per cent. NaCl solution, boiling carefully for 3 min., and then filtering. The colour intensity attains its maximum in 30 min. and remains unchanged for a further 90 min. The intensity is measured visually against a set of standards, or photometrically, with a red filter. G. S. SMITH

2366. **The oxidation of thallium (I) by selenous acid.** G. S. Deshmukh (*Anal. Chim. Acta*, 1955, **12** [4], 319–322).—When Tl^{I} acetate is boiled for 20 to 30 min. with an excess of H_2SeO_3 in 4 to 5 *N* HCl, quant. oxidation of Tl^{I} to Tl^{III} occurs. An equiv. quantity of Se is pptd.; this is filtered off in a porous porcelain or Gooch crucible, washed with cold water, ethanol and ether, dried for 20 min. at 90° C and weighed. The conversion factor (Se ≡ 2 Tl) limits the method to quantities of Tl > 20 mg. W. C. JOHNSON

2367. **Alkaline iodine as an oxidant for thallium (I).** G. S. Deshmukh (*Z. anal. Chem.*, 1955, **145** [4], 249–251).—Alkaline iodine is found to oxidise Tl^{I} to Tl^{III}. The hypoiodite acts as an oxidant, excess being converted into stable iodide and iodate by self-oxidation reduction. On acidification of the filtrate from the Tl^{III} the unchanged iodine is liberated quantitatively and titrated with thiosulphate. Results showed good agreement with those from other methods. R. J. MAGEE

2368. **Iodine monochloride end-point in the oxidation of thiocyanate by permanganate. Determination of cerium.** G. S. Deshmukh and M. K. Joshi (*Z. anal. Chem.*, 1955, **145** [5], 345–346).—This is a modification of the authors' earlier method (*Anal. Abstr.*, 1954, **1**, 2939). To a solution of $Ce(SO_4)_2$ add excess of KSCN till the yellow colour is completely discharged. Add sufficient HCl to give a concn. of 1·5 to 2 *N*, ICl (10 ml) and CCl_4 (5 ml), then titrate with standard $KMnO_4$. The presence of other tervalent rare earths does not affect the accuracy of the results. The method is applicable over a wide range of Ce concn. A table of results is given. R. STERN

2369. **Diphenylcarbazone as an internal indicator in mercurimetric analysis: the determination of cerium by potassium thiocyanate.** G. S. Deshmukh (*Z. anal. Chem.*, 1955, **145** [4], 251–253).—The quantitative oxidation of thiocyanate by ceric

sulphate has been studied and a method developed for the determination of small quantities of Ce by back-titrating the excess of unchanged KSCN with standard $Hg(NO_3)_2$ solution, with diphenylcarbazone as internal indicator. The end-point is sharp even in the presence of a strong acid medium and an excess of SO_4''. R. J. MAGEE

2370. **High-frequency induction furnace in the determination of radiocarbon.** A. M. Gaudin and H. E. Bergna (*Anal. Chem.*, 1955, **27** [3], 467–468).—An apparatus, in which mixtures containing ^{14}C compounds are ignited in O by heating in a high-frequency induction furnace, is described. The resulting CO_2 is examined by means of internally mounted Geiger counters. D. A. PANTONY

2371. **A new volumetric analysis of elementary carbon by decomposition with iodic acid in phosphoric acid.** T. Kiba, S. Ohashi, T. Takagi and Y. Hirose (*Japan Analyst*, 1953, **2** [5], 446–451).—It was found that elementary carbon is decomposed by heating with KIO_3 in conc. H_3PO_4 to give iodine and CO_2 ($5C + 4KIO_3 = 5CO_2 + 2K_2O + 2I_2$). (This method of decomposition can, with slight modifications, be applied to a variety of organic compounds.) The reaction starts at 100° C and ends at 150° to 230° C according to the sample, whilst the decomposition of KIO_3 itself starts at 250° C. Iodine equiv. in amount to the C is absorbed in a known excess of Na_3AsO_3 soln., which is titrated with 0·05 *N* iodine soln. A simple apparatus for this method was devised. Oxides of metals and non-metals do not react with KIO_3 under the given conditions. Chlorides, nitrates and ammonium salts should be absent. The results for graphite (both natural and artificial), active carbon, electrode carbon, etc., compared favourably with those obtained by the conventional combustion method; the causes of the errors are discussed. *Procedure*—The sample (5 to 15 mg) is placed in the reaction vessel together with KIO_3 (> twice the equivalent of the sample; 0·2 to 0·4 g). Conc. H_3PO_4 (3 to 4 ml) is added and the vessel is connected to the absorbing tube containing 0·1 *N* Na_3AsO_3 soln. (20·0 ml). A current of CO_2 is passed into the reaction vessel, which is heated gently (> 250° C) until the liquid becomes colourless. When the vessel cools below 100° C, the flow of CO_2 is stopped and water (10 ml) is added. The vessel is heated again for the iodine to distil into the absorption tube, which is eventually detached from the reaction vessel, and the contents are titrated with 0·05 *N* I soln., with starch soln. as indicator. K. SAITO

2372. **Determination of carbon and hydrogen in coal by the Sheffield high-temperature method.** R. A. Mott and H. C. Wilkinson (*Fuel, Lond.*, 1955, **34** [2], 169–184).—The latest form of apparatus and procedure for the determination of C and H in coal by the high-temp. method are described. Midvale tubes are used for both absorbents, a pressure gauge is included, and the exit end of the tube is lagged and provided with a heat-resistant bung. Results are given showing the agreement between four laboratories. In any laboratory, standard deviations of ± 0·10 per cent. for C and ± 0·025 per cent. for H should be obtained. The effects of rate of sample movement along the tube, ash, carbonate, sulphur and oxides of nitrogen are investigated. For high values of ash, S, N and carbonate the sample wt. should be reduced from 0·5 to 0·25 g, with 1 g of Al_2O_3. The method is simpler to operate, quicker and more accurate than the Liebig method. A. B. DENSHAM

2373. **Determination of carbon and hydrogen in coal: comparison of the Liebig and high-temperature methods.** L. J. Edgcombe (*Fuel, Lond.*, 1955, **34** [2], 185–190).—The C and H contents of sixteen coals (C contents 94 to 72 per cent. on a dry ash-free basis) were determined by the standard Liebig and the high-temp. methods. There is no significant difference in the results, but the latter method gives better reproducibility and is more rapid. A. B. DENSHAM

2374. **Determination of micro quantities of cyanide in presence of a large excess of sulphide.** M. O. Baker, R. A. Foster, B. G. Post and T. A. Hiett (*Anal. Chem.*, 1955, **27** [3], 448–449).—The sample (1 to 5 ml) containing 100 to 2500 μg of S'' and 1 to 10 μg of CN' is made up to 25 ml with 1 per cent. NaOH soln. (1 ml), glacial acetic acid (0·5 ml in excess of neutrality), bromine water (2 ml, or further quantities to dissolve S), As_2O_3 soln. (0·2 ml in excess of discharge of bromine colour), benzidine - pyridine reagent [pyridine (18 ml) dissolved in water (12 ml) and conc. HCl (3 ml), to which is added 1 per cent. benzidine in 0·5 *N* HCl (10 ml)] (4 ml), ethanol (5 ml) and, finally, water. The absorption is measured at 530 mμ *vs.* a reagent blank containing a S'' concn. similar to that of the sample. The reproducibility is given as ± 5 per cent. at the 10-μg level. D. A. PANTONY

2375. **Iodimetric determination of thiocyanates with arsenous acid.** B. R. Sant (*Chem. Ber.*, 1955, **88**, 581–583).—A simple volumetric determination of KSCN is based on the oxidation of iodine at pH 9 to 10, adjusted by a borax - boric acid buffer solution, and subsequent titration of excess of iodine with sodium arsenite. The buffer eliminates the interference of nascent HI and permits the reversible reaction $2I_2 + As_2O_3 + 2H_2O \rightleftharpoons 4HI + As_2O_5$ to become quantitative. Results (tabulated) agree with those obtained by Volhard's classical method. *Procedure*—A known vol. of dil. KSCN solution is treated with a known excess of iodine solution and 40 to 50 ml of borax - boric acid buffer (8 g of borax and 4 g of boric acid in 100 ml of H_2O). After standing in ice - water for ≃ 30 min, the excess of iodine is titrated with 0·1 *N* sodium arsenite, with starch as indicator. 1 ml of 0·1 *N* sodium arsenite ≡ 0·0012147 g of KSCN. S.C.I. ABSTR.

2376. **The determination of the purity of elementary silicon.** A. Mizuike and Y. Iida (*Japan Analyst*, 1953, **2** [5], 443–446).—The determination of Si in elementary Si by the gravimetric method is modified so as to calibrate the result by measuring the amount of Si (1 to 5 mg) which remains in the filtrate in the form of hydrated SiO_2. The filtrate and washings are combined, made slightly basic and heated on a water bath for 1 hr. to make the colloidal SiO_2 soluble. The soln. is made acidic and treated with ammonium molybdate and Na_2SO_3. The blue colour is compared with that of the standard soln. at 660 and 720 mμ. K. SAITO

2377. **Determination of silicon in fluorides by a spectrographic method.** M. M. Kosheleva and V. I. Chernetsova (*Zavod. Lab.*, 1955, **21** [4], 460–461).—The method was devised for determining silicon remaining in sodium and calcium fluorides prepared from fluorosilicic acid. Copper powder (0·9 g, 170 mesh) is mixed with 0·1 g of sample and compressed to give a 1-g pellet, then subjected to a condensed

spark between carbon electrodes. The line pair Si I 2516·123 and Cu I 2492·146 is measured. The standards are prepared either from mixtures of SiO_2 with CaF_2 and CaO or from mixtures of SiO_2 with NaF, Na_2CO_3 and NaCl. G. S. SMITH

2378. **The rapid determination of silicic acid in bauxite by the perchloric acid method.** K. Medicus (*Z. anal. Chem.*, 1955, **145** [5], 337–338).—An alternative method to that of F. W. Meier (*Zement*, 1932, **21**, 287, 305) for the determination of SiO_2 in bauxite is described. The acid mixture contains 14 vol. of dil. HCl (sp. gr. 1·09), 23 vol. of dil. H_2SO_4 (1·53) and 63 vol. of 60 per cent. $HClO_4$ (1·54). Add the acid mixture (20 ml) to powdered bauxite (0·5 g) and heat under reflux on a sand-bath, taking 40 min. from the beginning of boiling to the evolution of dense white fumes. Cool, add 10 per cent. HCl (25 ml) and digest for 5 min. on the sand-bath. Filter off the residue, wash with dil. HCl, ignite and weigh as SiO_2. Empirical corrections for different types of bauxite are given. This method has the advantage that it avoids evaporation with HF. It has been used as a sorting test for samples at the Unterlaussa mines. R. STERN

2379. **Spectrographic method for determining tin in ores.** M. A. Rivkina (*Zavod. Lab.*, 1955, **21** [4], 459–460).—The method described is suitable for determining 0·004 to 0·4 per cent. of Sn in ores containing large amounts of Fe, Si and Al, together with Ti, Cu, Pb and Zn, and sometimes In, Ga and Be. The material is diluted (1 + 1) with a buffer mixture of carbon powder with 10 per cent. of Na_2CO_3 and 1 per cent. of Sb_2O_5, the Sb acting as an internal standard. Carbon electrodes with an a.c. arc are used, and the line pairs Sn I 3034·12 and Sb I 2877·91, and Sn I 2839·99 and Sb I 2877·91 are measured. The probable error of a single determination is ± 8 per cent. G. S. SMITH

2380. **Micro-gravimetric determination of lead with [2-]mercaptobenzothiazole.** C. Cimerman and D. Bogin (*Anal. Chim. Acta*, 1955, **12** [3], 218–226).—Lead is pptd. with 2-mercaptobenzothiazole and the ppt. is heated with conc. aq. NH_3 soln. to convert it into the basic salt, $Pb(C_7H_4NS_2)OH$. *Procedure*—Heat 3 ml of the soln., containing 3 to 8 mg of $Pb^{\cdot\cdot}$, to boiling in a micro-beaker, hold the beaker in a bath of nearly boiling water and add, dropwise, a freshly prepared 1 per cent. soln. of 2-mercaptobenzothiazole in 2·5 per cent. aq. NH_3 soln. Stir after the addition of each drop of reagent soln. and use 0·142 to 0·226 ml of reagent soln. for each mg of $Pb^{\cdot\cdot}$ present (*i.e.*, a 76 to 180 per cent. excess). Remove the beaker from the water bath and, after 10 to 15 min., suck off the liquid from the ppt. with a porcelain filter-stick touching only the surface of the liquid. Remove the filter-stick and stir the ppt. for 2 to 3 min. with 0·4 ml of conc. aq. NH_3 soln. while the beaker is held in boiling water. Set aside for 5 min., filter with the filter-stick, and wash the ppt. with 2·5 per cent. aq. NH_3 soln. until the filtrate yields no ppt. with a 10 per cent. soln. of a cadmium salt. Determine the wt. of the ppt. after drying it at 110° C in the micro-beaker in a drying block with suction. Wt. of ppt. × 0·53608 = wt. of Pb. To provide an approx. and preliminary assessment of the amount of Pb present, the pptn. can be carried out on a titrimetric basis. W. C. JOHNSON

2381. **Polarographic analysis of heavy metals in sodium chloride of reagent grade. I. Determination of lead.** K. Sugihara and T. Saito (*Japan Analyst*, 1955, **4** [1], 27–30).—The quant. determination of a micro-amount of Pb, which consists in extraction with dithizone followed by polarography, is modified for the determination of Pb contents (≃ 0·0001 per cent.) in pure NaCl. The sample is dissolved in water (to 30 per cent. conc.) and the pH is adjusted to 9 with NH_4 citrate and aq. NH_3 soln. Lead is extracted with dithizone - CCl_4 soln. (20 mg per 100 ml) and transferred to an aqueous layer by shaking with HCl (1 + 1, 50 ml), which is evaporated with HNO_3 (2 × 2 ml) to decompose remaining traces of dithizone. The product is dissolved in water and submitted to polarography by the use of the supporting electrolytes, tartaric acid (0·1 *M*) and NH_4 acetate (0·5 *M*). Zinc (≃ 0·00001 per cent.) is simultaneously determined on the polarogram. K. SAITO

2382. **Reduction of nitroguanidine by titanium (III) chloride.** W. W. Brandt, J. E. DeVries and E. St. Clair Gantz (*Anal. Chem.*, 1955, **27** [3], 392–395).—A twenty-fold excess of 0·4 *N* $Ti^{\cdot\cdot\cdot}$ and of $Fe^{\cdot\cdot}$ in dil. (1 + 1) HCl is added to a known wt. of nitroguanidine under CO_2; the mixture is heated under reflux, cooled and titrated with standard $Fe^{\cdot\cdot\cdot}$ (SCN′ indicator). The reduction to guanidine and NH_3 is 98 per cent. quant., 8 equivalents of $Ti^{\cdot\cdot\cdot}$ having been consumed, allowance being made for a blank experiment. From these reductions, and examination of the similar reduction of nitrosoguanidine and of NO_3', a reaction sequence is proposed that involves a stepwise reduction, and explains the action of $Fe^{\cdot\cdot}$. D. A. PANTONY

2383. **Differentiation between rutile and anatase titanium dioxide.** R. S. Dantuma (*Verfkroniek*, 1955, **28** [2], 39–40).—Further trials with Dantuma's method (*Anal. Abstr.*, 1955, **2**, 60) indicate that it distinguishes clearly between rutile and anatase TiO_2, even with pigments that have been treated with alumina, etc., but the correlation with chalking properties is poor. D. R. DUNCAN

2384. **Thiocyanate spectrophotometric analysis of titanium, vanadium and niobium.** C. E. Crouthamel, B. E. Hjelte and C. E. Johnson (*Anal. Chem.*, 1955, **27** [4], 507–513).—Formation of thiocyanate complexes of Ti, Zr, Hf, V, Nb and Ta is critically examined. These elements are easily adjusted to the correct valency states and kept in solution in acidic media, but the elements in the IV and V valency states do not always react quant. within a reasonable time; the rates depend on the method of solution. Standard procedures for determination of Ti^{IV}, V^{III} and Nb^{V} are described, including special pre-treatment of samples to give uniform and correct colour development. Effects of variations of the colour-developing media—acid, salt, temp., miscible solvent and thiocyanate content—are discussed. D. R. GLASSON

2385. **Determination of small quantities of thorium by radioactivation.** E. N. Jenkins (*Analyst*, 1955, **80**, 301–313).—The method described consists in pile radiation of weighed amounts of the irradiated sample and a standard, dissolution of the irradiated sample and addition of a known amount (≃ 20 mg) of pure Th carrier as $Th(NO_3)_4$, purification of the ^{233}Th and carrier Th in a form suitable for beta-counting with an end-window Geiger counter, beta-counting with prolonged decay or aluminium absorption measurements, or both, to establish radiochemical purity and, finally, determination of

the chemical yield by a gravimetric assay as Th oxalate. Purification of the irradiated Th after addition of the carrier is effected chromatographically (Burstall *et al.*, *Brit. Abstr. C*, 1952, 95; Ryan *et al.*, *Ibid.*, 1952, 433; Kingsbury *et al.*, *Ibid.*, 1952, 430), and interference by Zr and U is prevented by a preliminary oxalate pptn. The final material for weighing and counting is a hydrated oxalate, $Th(C_2O_4)_2.8H_2O$, containing the 233 isotope in a high state of radiochemical purity. The half-life of ^{233}Th has been re-determined as 22·12 ± 0·05 min. A. O. JONES

2386. **Colorimetric estimation of thorium with quinalizarin.** A. Purushottam (*Z. anal. Chem.*, 1955, **145** [4], 245–248).—Thorium forms a coloured lake with quinalizarin in aqueous acetone which develops maximum colour in 60 to 70 per cent. acetone. The lake has a composition of thorium: dye (1 : 1), is stable and has a dissociation constant $3·76 \times 10^{-7}$. By this method 10 μg of thoria in 50 ml of solution can be determined. Cerite earths up to a 15-fold excess cause no interference. An absorption peak is obtained at 580 mμ.
R. J. MAGEE

2387. **A new method for the determination of a micro-amount of thorium.** M. Ishibashi and S. Higashi (*Japan Analyst*, 1955, **4** [1], 14–16).—A new colour reagent, *o*-arsonophenylazochromotropic acid (**I**), for the determination of a micro-amount of thorium, was synthesised and studied. *o*-Aminophenylarsonic acid (17 g) is dissolved in water (40 ml) and treated with HCl (sp. gr. 1·12, 30 ml) and 0·2 *N* $NaNO_2$ (5·0 ml). The diazo compound is filtered and added to an ice-cooled soln. containing chromotropic acid (3 g), Na_2CO_3 (4 g) and ether (2 to 3 ml). After 2 to 3 hr. it is neutralised with HCl to congo red and the pptd. **I** is recryst. with water. This reagent is sol. in water and reacts with Th at pH 1 to give a violet soln. (max. absorption 546 mμ), which is in accord with Beer's law up to 20 μg of Th per 10 ml. Zr and large amounts of Ti, Ce, UO_2^{++} and Fe^{+++} show similar colorations, and F' and PO_4''' interfere with the reaction. Th is co-pptd. with Al at pH 3·5 to 4·5, dissolved in dil. HNO_3 and extracted with *cyclo*hexanone at pH 0·65. Th is then transferred to an aqueous layer by shaking with water and submitted to colorimetric determination with **I**. K. SAITO

2388. **Estimation of thorium by organic reagents: recovery from worn-out gas mantles and tungsten filaments by 2:4-dichlorophenoxyacetic acid.** S. K. Datta and G. Banerjee (*Anal. Chim. Acta*, 1955, **12** [4], 323–328).—The demand for Th in various industries provides an interest in its possible recovery from wastes such as worn-out gas mantles and tungsten lamp-filaments. To determine Th in worn-out gas mantles the material is first dissolved in conc. H_2SO_4. The soln. is diluted with water and an aliquot containing ≃ 0·5 g of ThO_2 is brought to pH 2·8 to 3 by the addition of aq. NaOH soln.; 50 ml of hot 1·5 per cent. aq. 2:4-dichlorophenoxyacetic acid (**I**) are added and the soln. is warmed. The ppt. settles in 5 min.; it is filtered off, washed with hot 0·2 per cent. aq. **I**, then with hot water, ignited at 1000° C, and weighed as ThO_2. The results agree with those obtained by pptn. with *m*-nitrobenzoic acid and correspond to 89·5 per cent. of ThO_2 in the material. A similar method is used for the determination of Th in tungsten filaments after treating the filaments with aqua regia and filtering off the WO_3, but it is not entirely satisfactory for the determination of such low (≃ 1 per cent.) contents. W. C. JOHNSON

2389. **Separation of thorium from uranium by paper chromatography.** K. Suchý (*Chem. Listy*, 1954, **48** [7], 1084–1085).—Thorium (as Th^{++++}) and uranium (as UO_2^{++}) were readily separated by subjecting their aq. soln. to chromatography on Whatman No. 1 filter-paper; the two components were identified with aq. alizarin red S (pink - violet with Th, light blue with U), methanolic quinalizarin (clear blue with Th, light green with U), or a mixture of quinalizarin with $K_4Fe(CN)_6$ (light blue with Th, dark brown with U). The solvent systems used (with the component ratio of 7 : 2 : 1) and the R_F values for Th and U, respectively, were: methanol - pyridine - toluene, 0·16, 0·86 at 13° C; methanol - pyridine - dioxan, 0·13, 0·93 at 22° C; *n*-butanol - pyridine - dioxan, 0·07, 0·69 at 15·5° C; methanol - chloroform - toluene, 0·13, 0·72 at 20° C; pyridine - chloroform - toluene, 0·13, 0·45 at 19° C.
G. GLASER

2390. **Oxidation of hydrazine with selenous acid.** B. Suseela (*Chem. Ber.*, 1955, **88**, 23–25).—A new determination of hydrazine by oxidation with selenous acid is described, in which nitrogen is liberated and metallic selenium is precipitated. Hydrazine is determined by iodimetric titration of excess of selenous acid and weighing of the elementary selenium. A known excess of 0·1 *N* selenous acid is added to a measured vol. of hydrazine sulphate solution, whose content of hydrazine has been determined by the standard iodate method, and the acidity of the solution is raised to a concn. of 2 to 3 *N* by addition of H_2SO_4. After refluxing for ≃ 15 min., metallic selenium is precipitated, filtered off through a weighed crucible, washed and dried at 120° to 130° C. The excess of selenous acid in the filtrate and washings is determined iodimetrically with $Na_2S_2O_3$ and starch. The difference between the initial and final titration values corresponds with the vol. of reacted selenous acid expressed as thiosulphate, *i.e.*, with the amount of hydrazine. Results agree with those obtained by the usual iodate titration. The utilisation of this new method for determining phenylhydrazine and allied compounds is suggested. S.C.I. ABSTR.

2391. **Determination of hydroxylamine. A ferricyanide - cerimetric method.** B. R. Sant (*Z. anal. Chem.*, 1955, **145** [4], 257–260).—A ferricyanide - cerimetric method is presented for the quant. determination of hydroxylamine. The basis of the method is the oxidation of hydroxylamine to nitrogen by potassium ferricyanide in alkaline medium, with the formation, simultaneously, of ferrocyanide. To the hydroxylamine hydrochloride solution a measured excess (2 to 3-fold) of potassium ferricyanide is added, followed by 25 to 50 ml of borax - boric acid buffer (8 g of borax and 4 g of boric acid in 100 ml of water). This maintains a pH between 9 and 10, appropriate for the ferricyanide to act as an oxidant. The contents of the flask are swirled intermittently and set aside for about 20 min. The system is now acidified with HCl (1 + 1) or H_2SO_4 (1 + 5) and the resulting ferrocyanide is titrated with standard ceric sulphate, with ferroin or ferric chloride (near the end-point) as indicator. Results are in close agreement with those obtained by the classical bromate procedure.
R. J. MAGEE

2392. **Precipitation of pyrophosphate and triphosphate with tris(ethylenediamine)cobalt (III) chloride and hexamminocobalt (III) chloride.** H. W. McCune and G. J. Arquette (*Anal. Chem.*, 1955, **27** [3], 401–405).—The solubilities of certain cobalt-ammine phosphates, silicates and sulphates at various pH values are examined. In particular, tris(ethylenediamine)cobaltic chloride precipitates $H_2P_3O_{10}'''$ at pH 3·5, and HP_2O_7''' alone at pH 6·5, but some co-precipitation occurs with mixtures. Hexamminocobaltic chloride precipitates both P_3O_{10}'''' and P_2O_7'''', the yield increasing with increasing pH. The possible use of the reagents as amperometric titrating agents is examined and critically discussed. D. A. PANTONY

2393. **Determination of phosphate in perchloric and sulphuric acid solutions of uranium phosphates. Ion-exchange separation and amperometric determination.** E. G. Cogbill, J. C. White and C. D. Susano (*Anal. Chem.*, 1955, **27** [3], 455–457).—The soln. (5 ml) containing UO_2^{++}, SO_4'', ClO_4' and $\lesssim$ 25 mg of PO_4''' is neutralised with conc. aq. NH_3 (methyl red), the mixture is cooled and then made acid with conc. HNO_3 (5 ml) and boiled for 1 to 2 min. The soln. is diluted with water (300 ml) and passed through a cation-exchange column (25 cm × 2 cm of Dowex 50) to remove U^{VI}, and the eluate is made up to 500 ml with water washings. A 50-ml aliquot of this soln. is neutralised with 2 *M* NaOH (bromocresol green) and then made just acid with 0·1 *N* HCl, followed by 0·1 *N* acetic acid (0·5 ml). Ethanol (17 ml) and *M* KCl (7 ml) are added and the mixture is cooled. The soln. is titrated amperometrically with an applied potential of − 0·7 V *vs.* the S.C.E. with standard 0·035 *M* uranyl acetate. The average error is given as ± 0·5 per cent. D. A. PANTONY

2394. **New rapid method of analysis of slag for phosphorus, with a radioactive indicator.** A. I. Osipov, I. Yu. Kozhevnikov, V. E. Iudin, M. L. Sazonov, M. G. Bul'skiĭ, A. G. Alimov, A. M. Skreptsov and A. P. Ryabenko (*Zavod. Lab.*, 1955, **21** [4], 391–395).—The addition of a controlled amount of radioactive phosphorus, with a specific activity of 220 to 420 mC per g, to the melt in the manufacture of high-phosphorus (0·9 to 1·5 per cent.) cast iron, and measurement of the activity of portions of the slag after cooling in water to 30° to 40° C, permits the phosphorus content of the slag to be determined rapidly (within 5 to 7 min.) at any time during the course of the melt. To attain efficient mixing without loss of the radioactive phosphorus, the phosphorus is first mixed with iron powder and charged into a copper tube (150 mm × 18 mm), the ends of which are then sealed. The tube is placed in the liquid cast-iron. By the time the copper has melted, combination between the phosphorus and the iron has occurred, and uniform distribution throughout the mass of the metal takes place. Under the conditions of working, a proportionality factor for the distribution of phosphorus from the chemical analysis of a slag sample and its radioactivity is found and used for subsequent analyses. The error (average square error 6·2 per cent.) is less than that of normal chemical determinations. G. S. SMITH

2395. **The iodimetric determination of arsenic in ten-milligram amounts of organic compounds. II. Determination of arsenic in halogen-containing compounds; determination of antimony.** G. Bähr, H. Bieling and K.-H. Thiele (*Z. anal. Chem.*, 1955, **145** [2], 105–109).—The method formerly described (*Anal. Abstr.*, 1955, **2**, 598) has been applied to the determination of As in arsenic halides, organo-arsenic compounds with halogen attached to the As, with halogen attached to C, and with halogen in the anion. It has also been applied successfully to the determination of Sb in antimony halides and organo-antimony compounds. A. J. MEE

2396. **Amperometric determination of arsenic in mineral waters.** M. Kobrová (*Chem. Listy*, 1954, **48** [7], 1039–1042).—The following amperometric procedure for the determination of arsenic in mineral waters, by using short-circuited electrodes without applied voltage, gives accurate results with μg quantities of As. Evaporate the sample to dryness, neutralise the residue with a few drops of dil. H_2SO_4, dissolve the ferric hydroxide on the walls of the flask in a few drops of 6 *N* HCl and wash the soln. into a distillation flask with 6 *N* HCl (50 ml). To reduce As^V to As^{III}, treat the soln. with hydrazine sulphate (0·1 g) and KBr (0·03 g). Collect the distillate (40 ml), containing all the As as $AsCl_3$, in water (10 ml), add KBr (0·25 g) and titrate, using a rotating platinum electrode at 600 r.p.m. G. GLASER

2397. **The determination of niobium or tantalum in uranium and zirconium-base alloys.** G. W. C. Milner, G. A. Barnett and A. A. Smales (*Analyst*, 1955, **80**, 380–390).—A method is described for the determination of Nb and Ta in binary alloys with Zr, and for Nb in alloys of the type U - Zr - Nb. *Procedure*—The sample is digested with HNO_3 (25 ml) in a covered platinum dish on a hot-plate until attack ceases, 2 to 3 ml of 40 per cent. HF are added in drops, the mixture is warmed and more HF added if necessary. Any ppt. of uranium fluoride is ignored at this stage. Dil. H_2SO_4 (1 + 1) is added and the mixture is evaporated to incipient fuming with i.r. heating. To the cooled soln. 20 ml of 40 per cent. (w/w) HF are added and then 4 g of NH_4F, and the soln., when cool, is rinsed into a polythene separating funnel with 3·5 ml of dil. H_2SO_4 and finally with water until the vol. is 50 ml. The Nb or Ta is extracted with four 50-ml portions of *iso*butyl methyl ketone (hexone) which has been equilibrated with a soln. 10 *M* in HF, 6 *M* in H_2SO_4 and 2·2 *M* in NH_4F, all the extracts being combined in a polythene separator and washed with the equilibrating soln. (50 ml). (The construction of improvised polythene separators is described.) The Nb or Ta is extracted from the hexone with three 50-ml portions of diluted 100-vol. H_2O_2 (1 + 20), the combined extracts are evaporated by i.r. heating to fuming point with 10 ml of dil. H_2SO_4 (1 + 1) with precautions against loss by spraying. The cooled residue is treated with 10 ml of dil. HCl (1 + 1), followed by 40 ml of conc. HCl and 5 g of ammonium oxalate dissolved in a little water, and is rinsed into a beaker with water to a vol. of ≃ 100 ml and, after the pH has been adjusted to 4·5 by addition of aq. NH_3 in the presence of B.D.H. 4·5 indicator, is diluted to at least 250 ml with a pH 4·5 buffer prepared from *M* ammonium acetate - acetic acid. Tannic acid (1 g) is stirred in and the liquid is boiled for 2 min., then kept warm for 1 hr. The ppt. is collected on Whatman No. 40 paper, washed with a hot soln. containing 1 per cent. each of NH_4Cl and tannic acid and is finally ignited to Nb_2O_5 or Ta_2O_5. The filtrate is tested for complete pptn. by further digestion with 1 g of tannic acid. Recovery of Nb and Ta from alloys of known composition is good. A. O. JONES

2398. **Spectrophotometric determination of niobium in niobium-bearing steel.** J. L. Kassner, A. Garcia-Porrata and E. L. Grove (*Anal. Chem.*, 1955, **27** [4], 492–494).—Niobium in steel is determined colorimetrically by a procedure involving only two separations: hydrolytic pptn. by $HClO_4$ and extraction of the metal oxinate by $CHCl_3$. Most of the steel components are separable as sol. perchlorates from Nb, Ta, W, Si, Sn and Sb, which form insol. acids; Nb and Ta are quant. pptd. as the earth acids if H_2SO_3 is also present. Some Mo, Mn, V and B may be co-pptd. if originally present in large amounts, whilst the phosphates of Ti and Zr are very slowly sol. in $HClO_4$. These elements that may contaminate the niobic acid ppt. do not interfere, since some do not react with oxine and the remainder form oxinates which are insol. in $CHCl_3$ or are not extracted by $CHCl_3$ from the ammoniacal citrate solution. The yellow colour of solutions of Nb oxinate in $CHCl_3$ shows max. absorbance at 385 mμ and permits determination of 1·5 to 6·0 p.p.m. of Nb. Steel containing ≃ 0·75 per cent. of Nb is analysed with an accuracy of ± 1·3 per cent. (based on the amount of Nb). D. R. GLASSON

2399. **Titration of elementary sulphur with solutions of sodium cyanide.** D. A. Skoog and J. K. Bartlett (*Anal. Chem.*, 1955, **27** [3], 369–371).—An acetone soln., containing 10 to 80 p.p.m. of S, is diluted with one-fifth of its vol. of water and titrated (bromocresol purple) with 0·05 *N* NaCN in 80 per cent. aq. *iso*propanol that has been standardised against 0·05 *N* $AgNO_3$ in ammoniacal soln. (KI indicator), or against a standard soln. of S in acetone under the same conditions as in the determination procedure. The standard deviation is given as ± 0·2 per cent. Aliphatic sulphides and disulphides do not interfere, but mercaptans and cations that readily form complex cyanides give low results. D. A. PANTONY

2400. **Some notes on the rapid method for the simultaneous determination of sulphur and chlorine in coals and cokes.** R. Belcher and C. E. Spooner (*Fuel, Lond.*, 1955, **34** [2], 164–168).—Improvements are described in the high-temp. combustion method of Beet and Belcher (*Ibid.*, 1940, **19**, 42) for the determination of S and Cl in coal and coke. The sample wt. is reduced to 0·5 g, with an oxygen rate of 300 to 350 ml per min. A funnel-shaped silica adaptor fits through a bung into the outlet of the combustion tube, and its drawn-out end serves as the first of the two bubblers; this adaptor can readily be removed and washed out. The screened indicator should be made up fresh weekly. After titration of the total acid, excess of mercuric hydroxycyanide is added, and the alkali produced by reaction with Cl' is titrated. The accuracy of the titration may be increased by a "compensation titration," but this is justified only in the unusual instance of coal containing ≃ 1·0 per cent. of Cl. A. B. DENSHAM

2401. **Replacement of oxygen by carbon dioxide in the determination of sulphur in ores.** A. V. Dobrzhanskiĭ and V. I. Sakunov (*Zavod. Lab.*, 1955, **21** [4], 399–400).—Low results in the combustion method of determining sulphur in ores are due to the oxidation of part of the SO_2 formed to SO_3. It is shown that the use of carbon dioxide instead of oxygen gives SO_2 only, and that the theoretical titre of the iodine solution used for the determination gives the correct value for the sulphur content. Barium sulphate yields all its sulphur as SO_2 when ignited at 1300° C in a stream of carbon dioxide. G. S. SMITH

2402. **A method of determining sulphate ion with the aid of ion-exchange resins.** M. Honda and H. Tadano (*Japan Analyst*, 1953, **2** [5], 451–456).—Sulphate ions adsorbed by Amberlite IR-4BA (Cl or OH) are eluted with NaOH soln. (≃ 0·2 *N*) and the eluate is passed through a column of cation-exchange resin. The final eluate consists of HCl and H_2SO_4 and is titrated successively with NaOH and $AgNO_3$ soln. to give the amount of SO_4''. Experimental conditions for the adsorption of SO_4'', for the removal of other anions from the column with HCl and for the elution of SO_4'' by NaOH soln. were investigated. Common cations, except Cr^{++}, do not interfere with the method provided that they are removed by passing the soln. through a cation-exchange resin before the adsorption of SO_4'' by Amberlite IR-4BA. This method is suitable for the determination of SO_4'' in common salt. K. SAITO

2403. **Polarographic determination of sulphite.** D. B. Aulenbach and J. L. Balmat (*Anal. Chem.*, 1955, **27** [4], 562–564).—Sulphite is determined polarographically in the presence of other reduced compounds in the study of sulphur transformations in biological sewage treatment. The sample is de-aerated under neutral or alkaline conditions and then acidified to convert all the sulphite into SO_2. The difference between the heights of the anodic waves before and after desorption of SO_2 is directly proportional to the original concn. of sulphite. The method is sensitive to at least 1 p.p.m. of sulphite S; samples containing > 200 p.p.m. require too long for complete desorption. Only sulphide and thiosulphate interfere and, after their removal by Mangan's method, the sulphite is determined to an accuracy of ± 4 per cent. D. R. GLASSON

2404. **Determination of very small quantities of chromium in hydrochloric acid solution.** W. Oelschläger (*Z. anal. Chem.*, 1955, **145** [2], 81–88).—The method uses the coloration formed between Cr^{VI} and diphenylcarbazide. Cr^{III} can be satisfactorily oxidised to Cr^{VI} by $(NH_4)_2S_2O_8$ - NaOH, or H_2O_2 - NaOH. The process is best carried out in diffuse daylight or in the dark, as the colour is rapidly bleached in sunlight. Small amounts of Mn do not interfere. A. J. MEE

2405. **Determination of chromium and vanadium in fast-cutting steel.** B. E. Jaboulay (*Chim. Anal.*, 1955, **37** [3], 97–99).—Two alternative procedures are described for the determination of 3 to 6 per cent. of Cr and up to 5 per cent. of V in steel that also contains W, Mo and Co. The sample is prepared either by boiling with H_2SO_4, HNO_3 and $KMnO_4$, and filtering through asbestos, or by heating to fuming with $HClO_4$ and HNO_3, and boiling with dil. HCl. The V and Cr are determined, stepwise, by $FeSO_4$ - $KMnO_4$ titrations in H_3PO_4 soln., with the use of the $KMnO_4$ colour for the chromate end-point, and Ba diphenylamine-sulphonate as indicator for the vanadate titration. A. R. ROGERS

2406. **Determination of molybdenum by paper chromatography.** G. Almássy and J. Straub (*Magyar Kém. Foly.*, 1954, **60** [4], 104–106; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 50,213).—For the separation of Mo^{VI} from other elements, 96 per cent. ethanol - conc. HCl. soln. - water (40:10:50) is used as solvent. The error is ±

20 per cent. and the sensitivity limit is 0·1 μg of Mo in 0·1 ml of soln. For Mo$^{\cdots\cdots}$ the R_F value is 0·58; for Sr$^{\cdot\cdot}$, Ca$^{\cdot\cdot}$, Ba$^{\cdot\cdot}$, Au$^{\cdot\cdot\cdot}$, Fe$^{\cdot\cdot\cdot}$, Cr$^{\cdot\cdot\cdot}$, Al$^{\cdot\cdot\cdot}$, Ti$^{\cdot\cdot\cdot\cdot}$, Bi$^{\cdot\cdot\cdot}$, As$^{\cdot\cdot\cdot}$, Cu$^{\cdot\cdot}$, Zn$^{\cdot\cdot}$, Sb$^{\cdot\cdot\cdot}$, V$^{\cdot\cdot\cdot\cdot}$, Co$^{\cdot\cdot}$, Ni$^{\cdot\cdot}$, Mg$^{\cdot\cdot}$, Cd$^{\cdot\cdot}$, Th$^{\cdot\cdot\cdot\cdot}$, Mn$^{\cdot\cdot}$, $UO_2^{\cdot\cdot}$, Hg$^{\cdot\cdot}$ and Sn$^{\cdot\cdot}$ it is within the range 0·77 to 0·91. Extraneous ions do not affect the sensitivity. E. HAYES

2407. **The indirect complexiметric determination of molybdenum.** A. de Sousa (*Anal. Chim. Acta*, 1955, **12** [3], 215–217).—A rapid method is described for the determination of Mo in solutions free from WO_4'', oxalate, SO_4'' and PO_4'''. *Procedure*—To 100 ml of the soln., containing $\simeq$ 100 mg of Mo as Na_2MoO_4, add 10 ml of saturated aq. $CaCl_2$ soln., boil for a few min., then cool. Filter off the ppt. and wash it 3 to 5 times with aq. $CaCl_2$ soln. (1+ 10) and then 2 to 3 times with cold water, dissolve it in warm (50° to 60° C) dil. HCl (1 + 1), evaporate the soln. to dryness and heat the residue on a sand-bath for 1 hr. Extract the residue by stirring with water at $\simeq$ 50° C, filter, and wash the filter with warm water. Evaporate the filtrate, if necessary, to 200 ml, add aq. NaOH soln. to produce a pH > 12 and, with murexide as indicator, titrate with 0·1 *M* EDTA (disodium salt), of which 1 ml $\equiv$ 9·6007 mg of Mo. W. C. JOHNSON

2408. **Polarographic determination of molybdenum in ores.** S. Yokosuka (*Japan Analyst*, 1953, **2** [4], 319–322).—A polarographic analysis of Mo in ores (rapid in comparison with that involving the pptn. of sulphide) was studied in a controlling soln. of phosphoric acid. The interference of V is eliminated by the addition of tartaric acid, and that of Cr and As by treatment with H_2O_2. A small amount of methyl red surpresses the max. of the waves of Cu and Fe; Pb and Cd must be removed by the usual pptn. method. The determination of 0·3 to 5 per cent. of Mo in various ores can be effected in $\simeq$ 7 hr. *Procedure*—The sample (0·5 to 1 g) is fused with KOH (7 g), extracted with water and filtered. The filtrate is neutralised with H_3PO_4 and treated with a further 20-ml portion of H_3PO_4 (sp. gr. 1·8) and a small amount of H_2O_2. After the removal of excess of oxygen, tartaric acid (5 g) and 1 per cent. methyl red soln. (1 ml) are added and the whole is made up to 100 ml. This soln. is submitted to polarography and the wave height of Mo ($E_{\frac{1}{2}}$ – 0·44 V *vs.* the S.C.E.) is compared with that of the standard. When Pb and Cd are present, the sample is decomposed with HCl and HNO_3, and converted into sulphates with dil. H_2SO_4 (1 + 1) (50 ml). $PbSO_4$ is filtered off and the filtrate is neutralised with K_2CO_3 soln. (10 per cent.). A further 10 ml of K_2CO_3 soln. is added and $CdCO_3$ is filtered off. The filtrate is then treated as described above. K. SAITO

2409. **Method of analysis of tungsten chlorides.** S. A. Shchukarev, G. I. Novikov and N. V. Andreeva (*Zavod. Lab.*, 1955, **21** [4], 401–403).—It is shown that WCl_6 boiled with water, or heated in an atmosphere containing water vapour, is completely hydrolysed and can be determined from the amount of HCl produced. The material is placed in a crucible supported inside and near the closed end of an inverted test-tube. The open end of the test-tube stands in a beaker containing a standard alkali solution. An electric heater round the closed end is available for heating the crucible to 150° to 200° C. The top of the crucible carries a capillary tube partly filled with water. When the heater is switched on, the water is forced into the crucible by the expansion of air in the capillary. After being heated for 1 to 1·5 hr. the crucible is removed and ignited in a muffle-furnace to give the weight of WO_3. Any residue on the walls of the test-tube is washed into the alkali soln. and the chloride is determined. The method is suitable also for the lower chlorides of tungsten and for many other hydrolysable chlorides. The apparatus can be used to remove and determine ammonium chloride in ammoniacal solutions of WCl_6. G. S. SMITH

2410. **A selective procedure for the gravimetric estimation of uranium as oxinate using Complexone as masking agent.** R. N. S. Sarma and A. K. Mallik (*Anal. Chim. Acta*, 1955, **12** [4], 329–334).—In the gravimetric determination of $UO_2^{\cdot\cdot}$ with oxine, disodium ethylenediaminetetra-acetate (**I**) is added to prevent interference from a number of metals that are normally pptd. A $UO_2(NO_3)_2$ soln. containing $\simeq$ 30 mg of U and an added quantity of another metal is neutralised (yellow to methyl red) with aq. NH_3 and is treated with 3 to 10 ml of a 10 per cent. aq. soln. of **I**. The soln. is buffered at $\simeq$ pH 5·3 by adding 1·1 ml of dil. acetic acid (1 + 1) and 25 ml of 20 per cent. aq. NH_4 acetate; it is then diluted to 150 to 175 ml, heated to 70° C and 5 ml of 4 per cent. ethanolic soln. of oxine are added dropwise. After a few min. in a water bath at 30° C the soln. is allowed to cool to room temp.; the ppt. is filtered off in a sintered-glass crucible (No. 3), washed with warm 0·01 per cent. oxine soln. (prepared by diluting 1 ml of 4 per cent. ethanolic soln. with 400 ml of water), dried at 100° C for 1 hr., and weighed. The rare earths and Th, Cd, Zn, Pb, Bi, Mn, Co and Ni may each be present at several times the U concn. without interfering, but Al, Fe$^{\cdots}$ and Cu interfere when present in concn. $\simeq$ the concn. of U. When Zr is present in a 2 to 3-fold excess, 7 to 8 ml of oxine soln. must be used. When PO_4''' is present, aq. **I** (10 ml) and oxine soln. (7·5 ml) are added first, the soln. is heated to 70° C, neutralised (yellow to thymol blue) with aq. NH_3 and 25 ml of aq. NH_4 acetate are added dropwise. When MoO_4'', VO_3' or WO_4'' are present, aq. **I** (10 ml) and aq. NH_4 acetate (10 ml) are added first, the soln. is diluted to 150 ml, heated to 70° C, neutralised (just pink to phenolphthalein) with aq. NH_3, and treated with 5 ml of oxine soln. W. C. JOHNSON

2411. **High-frequency titrations involving chelation with ethylenediaminetetra-acetic acid. III. Determination of uranyl ion.** R. Hara and P. W. West (*Anal. Chim. Acta*, 1955, **12** [3], 285–291).—When solutions of a $UO_2^{\cdot\cdot}$ salt and EDTA (**I**) are mixed, the resulting solutions are more acid than either of the original solutions. High-frequency titrations (*Anal. Abstr.*, 1955, **2**, 9; 1226), with NaOH soln., of such mixtures indicate that at a $UO_2^{\cdot\cdot}$:**I** ratio of 2:1 a chelate is formed, though this chelate is less stable than the 1:1 chelates commonly formed by heavy metals. Uranyl solutions (0·002 to 0·0003 *M*), adjusted to pH 3·5 to 4·0, are titrated with solutions of the trisodium salt of **I** (0·02 to 0·003 *M*) with the use of a Sargent Model V Oscillometer, and a max. error of 0·92 per cent. is recorded. Ba$^{\cdot\cdot}$, Sr$^{\cdot\cdot}$, Ag$^{\cdot}$ and Tl$^{\cdot}$ do not influence the reaction; other heavy metals, acetate and oxalate interfere; sulphate reduces the sharpness of the end-point. W. C. JOHNSON

2412. **Microchemical detection of fluorides. Sodium fluorosilicate crystal test.** N. I. Goldstone (*Anal. Chem.*, 1955, **27** [3], 464–466).—The sample

containing > 0·4 μg of F′ is ignited to 500° C to remove org. matter, and the ash is extracted with water; Cl′ and CO_3'' are removed by pptn. with solid Ag_2SO_4. The suspension is filtered and the filtrate evaporated with $CaCO_3$ (0·5 g) and SiO_2 (2 mg) to dryness. After being cooled, the mixture is warmed with conc. H_2SO_4 (2 drops) and the distillate is collected in a hanging drop of water. After drying, the drop site is examined microscopically for characteristic crystals of Na_2SiF_6 and compared with an authentic specimen. Fluoroacetic acid does not interfere, but fluorine–carbon bonds may be detected by this test after a preliminary fusion with Na_2CO_3. D. A. PANTONY

2413. **Pyrohydrolysis in the determination of fluoride and other halides.** J. C. Warf, W. D. Cline and R. D. Tevebaugh (*Anal. Chem.*, 1954, **26** [2], 342–346).—A current of steam is passed over the fluorides in a platinum apparatus at 1000° C. The condensate, containing HF, is titrated with 0·1 *M* NaOH and the residual metal oxide is weighed. Fluorides of heavy metals and Mg are completely hydrolysed within 20 min. Light-metal fluorides and alkali fluoride complexes are very slowly hydrolysed and must be aided by an accelerator; U_3O_8 was best for this purpose. The addition of U_3O_8 decreased the precision from within 0·05 per cent. to within 0·5 per cent. CHEM. ABSTR.

2414. **Apparatus for the pyrohydrolytic determination of fluoride and other halides.** C. D. Susano, J. C. White and J. E. Lee, jun. (*Anal. Chem.*, 1955, **27** [3], 453–454).—An apparatus, constructed mainly of nickel and stainless steel, for the determination of halides by decomposing them with steam at 1000° C (*cf. Anal. Abstr.*, 1955, **2**, 2413), is described. Cost, durability and ease of manipulation are claimed to be satisfactory. D. A. PANTONY

2415. **New colorimetric determination of small quantities of fluoride by using *p*-dimethylaminoazobenzenearsonic acid zirconium lake.** M. Kamada, T. Onishi and M. Ota (*Bull. Chem. Soc. Japan*, 1955, **28** [2], 148–149).—A colorimetric method is described for the determination of less than 1 p.p.m. of F′ in aq. soln. Quantities as small as 0·01 p.p.m. may be detected. A 10-ml sample soln. containing less than 1 p.p.m. of F′ and a corresponding 10-ml standard F′ soln. are placed in matched tubes, and 2 ml of 6 *N* HCl and 1 ml of the suspended lake reagent are added to each; the tubes are shaken and set aside at room temp. for 1 hr. The filtered soln. are then compared spectrophotometrically. Interfering substances include thiosulphate, sulphide, nitrite, cyanide, chromate, sulphite, permanganate, sulphate, borate, Al, Sb, Sn, Cd and Fe, and a large number of organic compounds. The suspended lake reagent is prepared by adding a soln. of 100 ml of 6 *N* HCl containing 0·1 g of $ZrOCl_2.8H_2O$ to a soln. of 100 ml of 6 *N* HCl containing 0·2 g of *p*-dimethylaminoazobenzenearsonic acid; this mixture is set aside for 30 min. at room temp., then centrifuged and the supernatant liquid is decanted; the residue is repeatedly washed with 2 *N* HCl, and finally suspended in 200 ml of *N* HCl soln. The lake reagent is stable for several weeks if kept in the dark. G. R. WHALLEY

2416. **Determination of fluorine in chrome-plating baths containing fluorides.** T. Higashino and S. Musha (*Japan Analyst*, 1955, **4** [1], 3–8).—A new method for the determination of fluorine in various chrome-plating baths is proposed. Fluorine is determined colorimetrically by the aluminium-aluminon method (R. E. Osherovich, *Zavod. Lab.*, 1938, **7**, 934), subsequent to the removal of Cr··· with the aid of a cation-exchange resin. No marked interference results from the presence of ions other than SiO_3'' (> 2·6 mg per ml) and C_2O_4'' (> 0·15 mg per ml). *Procedure*—The sample (10 ml, 0·2 to 5 mg of F′ per litre) is diluted to 750 ml and a 5-ml portion is treated with ethanol (2 ml) and *N* HCl (3 ml) on a water bath for 5 min. to reduce Cr_2O_7'' to Cr···. It is then passed through a column of Daiya Ion K (R-H form), which is subsequently washed three times with water (20 ml). The eluate is neutralised to phenolphthalein with NaOH and treated with Al··· soln. (40 mg per 5 ml), *N* HCl (8 ml), 3 *N* NH_4 acetate (5 ml), 0·1 per cent. aluminon soln. (5 ml) and 6 *N* $(NH_4)_2CO_3$ (0·5 ml). The whole is made up to 100 ml and the light extinction is measured after 45 min. The average deviation from the mean is about 2 per cent. K. SAITO

2417. **Polarographic determination of traces of fluoride and iron.** C. E. Shoemaker (*Anal. Chem.*, 1955, **27** [4], 552–556).—A method for determining microgram quantities of fluoride and Fe in the presence of radioactive substances is developed. Active O and peroxides, formed in aq. solution by intense radioactivity, attack dye and fluorescent salts used in conventional analytical methods for F′. Rotating platinum micro-electrodes are used, the F′ giving a complex with the Fe··· which is reduced irreversibly at potentials more negative than for the reduction of Fe···; a value of $6{\cdot}9 \times 10^{-5}$ is obtained for the dissociation constant of $FeF^{··}$. One microgram of F′ and 0·33 μg of Fe are determined to an accuracy of ± 15 per cent. D. R. GLASSON

2418. **Colorimetric determination of chloride ion via ion exchange.** J. L. Lambert and S. K. Yasuda (*Anal. Chem.*, 1955, **27** [3], 444–446).—A 50-ml burette is packed with 6 cm of granular $AgIO_3$ (preparation described) which is washed twice with the soln. containing Cl′. The burette is filled to the zero mark with the test soln., and exactly 10 ml are run out and made up to 100 ml. A 10-ml aliquot of this soln. is made up to 250 ml, and 20 ml of it are treated with *N* HCl (1 ml) and 1·1 per cent. CdI_2 - 0·25 per cent. potato-starch reagent (1 ml). Absorption is measured at 615 mμ after 5 min. of mixing. The Cl′ concn. (0 to 180 p.p.m. in the final soln.) is determined from standards. Results of the analysis of 3 domestic or river waters are presented and compared with those from standard methods. Of 16 ions commonly encountered in water analysis, $NH_4^{·}$, $Ca^{··}$, Al··· and Fe··· interfere. D. A. PANTONY

2419. **Micro-determination of chloride by the diffusion technique, and the chloride content of raw cotton.** H. Naylor (*Shirley Inst. Mem.*, 1955, **28** [9], 123–130).—Conway's method (*Biochem. J.*, 1935, **29**, 2221) for the micro-determination of chloride is improved by absorbing the Cl in Na_3AsO_3 instead of KI, thus eliminating error due to the volatilisation of I. In the analysis of cotton, the sample is moistened with Na_2CO_3 solution and ignited. The neutralised ash and washings are sucked into the outer compartment of the apparatus and evaporated to dryness. The residue is treated with powdered $KMnO_4$ and dil. H_2SO_4 and the Cl which is expelled is absorbed in a measured vol. of 0·05 *N* Na_3AsO_3 solution in the inner compartment of the apparatus.

After 18 hr. the residual arsenite is titrated with 0·05 *N* iodine solution in the presence of starch.
A. M. SPRATT

2420. **The detection of bromate ion by the use of a manganese salt.** H. Fukamauchi and S. Obata (*Japan Analyst*, 1955, **4** [1], 25–26).—It is generally understood that BrO_3' reacts with Mn$^{\cdot\cdot}$ to give MnO_2 and Br_2, but ClO_3' does not (A. Monnier, *Ann. Chim. Anal.*, 1916, **21**, 239). It has now been found that ClO_3' is capable of undergoing this reaction, but at a low velocity. The method of detecting BrO_3', which makes use of the oxidation of Mn$^{\cdot\cdot}$ to MnO_2 and the coloration of benzidine by MnO_2, can be modified by detecting Br (vapour) with an ethanolic soln. of fluorescein or Schiff's soln. (limit of detection, 13 μg per 0·25 ml). K. SAITO

2421. **Iodimetric studies. I. Determination of iodic acid in the presence of chloric and bromic acids.** L. Szekeres (*Magyar Kém. Foly.*, 1954, **60** [4], 108–110; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 50,227).—A mixture containing $HBrO_3$, $HClO_3$ and HIO_3 is reduced with HBr in HCl soln. and then treated with an excess of $NaHCO_3$; any NaIO formed is oxidised by NaClO or NaBrO to $NaIO_3$. Sodium hypochlorite and NaBrO are then selectively reduced by urea, ethanol or sodium formate, and the $NaIO_3$ is determined iodimetrically.
E. HAYES

2422. **A rapid determination of manganese in iron and steel by a persulphate - oxalate method.** T. Ikegami and T. Nagaoka (*Japan Analyst*, 1953, **2** [4], 328–331).—The rapid determination of Mn in iron and steel by titration with Na_3AsO_3 standard soln., subsequent to the oxidation of Mn with $(NH_4)_2S_2O_8$, involves the use of an empirical factor for the arsenite soln. This can be avoided by titrating with Na oxalate soln. in the presence of H_3PO_4. $KMnO_4$ is stabilised by the PO_4''' so that no appreciable decomposition takes place during the decomposition of excess of persulphate by boiling. Cr (< 1 per cent.) and V (< 1 per cent.) do not affect the result. The time occupied by an estimation is < 15 min. *Procedure*—The sample (0·25 to 2 g) is decomposed by a mixed acid (conc. H_2SO_4, 85 ml, conc. HNO_3, 40 ml, and water, 850 ml) (60 ml), treated with H_3PO_4 (sp. gr. 1·7) (5 ml), $AgNO_3$ (1 per cent.) (10 ml) and $(NH_4)_2S_2O_8$ (2 g) and boiled with 150 ml of water for 7 min. Cold water (50 ml) is added and the purple soln. is titrated with 0·1 *N* Na oxalate soln.
K. SAITO

2423. **Quantitative spectrochemical analysis of manganese in [mineral] pulps and rocks by flame photometry.** R. Ishida (*Rep. Gov. Chem. Res. Inst. Tokyo*, 1955, **50** [1], 35–39).—The analysis of Mn by the use of flame spectra in an acetylene - air flame was studied. Compressed air is bubbled through the sample soln. which is then burnt in an acetylene flame. The spectra are taken on a photographic plate and the intensity is compared with that of the standard. The working curve is a straight line within the range 10^{-4} to 10^{-2} mole of Mn per litre (Mn 4030·8 Å). No significant interference results from the presence of common ions in the sample soln. Pulp samples (100 to 500 g) are ashed at as low a temp. as possible and dissolved in dil. HCl. Rock samples are decomposed with H_2SO_4 - HF or $HClO_4$ - HF mixture and dissolved in dil. HCl. K. SAITO

2424. **Cacotheline as a reagent for the detection of ferrous and ferric iron.** G. G. Rao, V. N. Rao, G. Somidevamma and K. Lalita (*Anal. Chim. Acta*, 1955, **12** [3], 271–279).—Cacotheline is not normally reduced by Fe$^{\cdot\cdot}$ but, in the presence of F$'$ or oxalate, reduction takes place with the production of a blue colour at pH > 5·2 or a pink colour at pH < 4·58. These colours are unstable, but the max. stability is obtained at pH 3·49 to 4·58. To detect Fe$^{\cdot\cdot}$, 5 ml of Na acetate - HCl buffer soln. (pH ≃ 3·5 to 4·0) are mixed with 0·2 ml of 0·25 per cent. cacotheline soln. and 2 ml of 0·1 *N* Na oxalate, and 0·5 ml of the test soln. is added. The limiting concn. is 1:40,000 and the limit of detection is 1·5 μg. For the lower concn. of Fe$^{\cdot\cdot}$, a 0·025 per cent. soln. of the reagent is used. Certain oxidising anions and Sn$^{\cdot\cdot}$ interfere; Mn$^{\cdot\cdot}$, Ni$^{\cdot\cdot}$, Cr$^{\cdot\cdot\cdot\cdot}$ and Co$^{\cdot\cdot}$ render the colour less stable. If Fe^{III} is present, it can be reduced to Fe^{II} in the presence of the buffer and oxalate by exposure to sunlight; the colour reaction is then produced on the addition of cacotheline. W. C. JOHNSON

2425. **A micro-heterometric determination of traces of iron (III) in alloys and salts with 1-nitroso-2-naphthol.** M. Bobtelsky and E. Jungreis (*Anal. Chim. Acta*, 1955, **12** [4], 351–357).—Solutions of Fe$^{\cdot\cdot\cdot}$ (0·07 to 0·2 mg in 20 ml) are made 0·01 *N* with respect to HCl and are titrated with a 0·01 to 0·005 *M* ethanolic soln. of 1-nitroso-2-naphthol, the end-point being determined by the heterometric method (*Anal. Abstr.*, 1954, **1**, 29, 51). The titration occupies ≃ 1 hr. and can be carried out in the presence of relatively high concn. of Ca$^{\cdot\cdot}$, Ba$^{\cdot\cdot}$, Mg$^{\cdot\cdot}$, Zn$^{\cdot\cdot}$, Al$^{\cdot\cdot\cdot}$, Cr$^{\cdot\cdot\cdot}$, Cd$^{\cdot\cdot}$, Mn$^{\cdot\cdot}$, Ni$^{\cdot\cdot}$ or Pb$^{\cdot\cdot}$. Citrate and tartrate must be absent. The max. error is 4 per cent. W. C. JOHNSON

2426. **Studies on organic analytical reagents. VII. Ferrous complex salts of benzothiazole-2-carboxylic acid.** K. Yoshikawa and K. Shinra (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [11], 1220–1223).—The stoicheiometric relation of the ferrous complex of benzothiazole-2-carboxylic acid (**I**) and its visible absorption spectrum were studied in aq. and ethanolic soln. The molar ratio of Fe$^{\cdot\cdot}$ to **I** is 1:3 in ethanolic soln. and 1:2 in the crystalline state, whilst the ratio is 1:1 in aq. soln. (also in a soln. of KCN), showing different results from those for quinaldic and picolinic acids (both 1:3 in aq. soln.). The absorption spectrum of the complex in aq. soln. (max. absorption 440 mμ) is subject to a bathochromic effect on the addition of ethanol (465 mμ) or KCN (482·5 mμ in 1 *M* KCN). The extinction coeff. is proportional to the concn. of Fe$^{\cdot\cdot}$ (up to 3×10^{-3} *M*) in either aq. or ethanolic soln. K. SAITO

2427. **Colorimetric determination of iron with dimethylglyoxime. I. The use of pyridine as the base.** N. Oi (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [10], 1067–1069; 1069–1070).—Tschugaeff's method of determining Fe$^{\cdot\cdot}$ (*Z. anorg. Chem.*, 1914, **89**, 401) with dimethylglyoxime (DG) was modified by the use of pyridine (Py) instead of NH_3. The complex $[Fe(DG)_2.2Py]$ gives an intense colour (max. absorption 500 mμ) in an ammoniacal soln. containing Na tartrate and hydroxylamine, which remains unchanged for > 24 hr. The use of other organic amines, including methylamine and collidine, was not found to be better than pyridine. The extinction coeff. is proportional to the concn. of Fe$^{\cdot\cdot}$ up to 200 μg per 50 ml. **II. Determination of iron by extraction with organic solvents.** The coloured complex $[Fe(DG)_2.2Py]$ can be extracted with various organic solvents from an ammoniacal soln. containing pyridine. The absorption spectrum

of the chloroform extract is almost identical with that of the aq. soln. (max. absorption 500 mμ). Its extinction follows Beer's law up to 50 μg of Fe^{++} per ml of $CHCl_3$, and can be used for the micro-determination of Fe^{++} in the presence of Cu (< 25 μg), Co (< 20 μg), Mn (< 50 μg), Zn (< 500 μg), Ti (< 10 mg) and Al (< 30 mg). Ni and Pb should be absent. K. SAITO

2428. **A rapid colorimetric determination of iron in Babbitt metal.** K. Ota (*Japan Analyst*, 1953, **2** [5], 439–442).—Iron (< 0·2 per cent.) in Babbitt metal can be analysed colorimetrically with sulphosalicylic acid after removing tin and antimony bromides by evaporation. Other components of the alloy, including Cu (< 9 per cent.), Pb, Bi, Ag, Zn and Cd, do not interfere. The time occupied by an estimation is < 1·5 hr. *Procedure*—The sample (0·5 to 1 g) is dissolved in H_2SO_4 (if turbid, filter), transferred to a 100-ml flask and heated at 200° to 220° C. HBr is dripped into the vessel and the bromides of Sn and Sb are volatilised in a current of air. The residue is treated with HNO_3 (1 ml) and heated until white fumes of H_2SO_4 are evolved. After being cooled, the soln. is diluted and dil. aq. NH_3 is added to give a pH of 2·0 to 2·4. Sulphosalicylic acid (10 per cent.) (5 ml) is added and the whole is made up to 250 ml. The extinction is measured at 500 mμ and the content of Fe calculated. K. SAITO

2429. **Mercurimetric determination of iron in ores.** D. N. Finkel'shtein and G. N. Kryuchkova (*Zavod. Lab.*, 1955, **21** [4], 403–405).—*Procedure*—Iron ore (0·2 g) is heated with 5 ml of HCl and then with 2 to 3 ml of HNO_3 and 3 to 5 drops of HF. With a high silicate content the HF addition is repeated. After decomposition of the ore, 10 ml of dil. (1 + 1) H_2SO_4 are added and the solution is evaporated until fumes are evolved. The cooled solution, diluted to 150 ml, is treated with 5 ml of 20 per cent. NH_4SCN solution and titrated with 0·05 *N* $HgNO_3$ within 5 min. If more than 25 ml are required, another 5 ml of thiocyanate are added before the titration is continued. If the ore contains more than 0·4 to 0·5 per cent. of Cu, the Fe must first be separated by pptn. with aq. NH_3. Molybdate, Al^{+++}, Cd^{++} and Zn^{++} do not interfere in any amounts, but with large amounts of Zn (≮ 0·3 g) the pptd. $ZnHg(SCN)_4$ tends to absorb Fe unless the titration is carried out very slowly, with vigorous shaking near the equivalence point. Vanadate up to 0·5 mg and fairly large amounts of Pb^{++}, Ni^{++}, Co^{++} and Cr^{+++} do not interfere. Strong oxidising agents must be absent. G. S. SMITH

2430. **Rapid methods of solution with hydrogen peroxide. I. Dissolution of iron, steel and ferro-alloys.** K. Kawamura (*Japan Analyst*, 1953, **2** [4], 347–354).—A mixture of H_2O_2 and mineral acids, HF, $HClO_4$, oxalic acid or citric acid enables a rapid dissolution of iron and steel with or without heating. The times required for the solution of various steels and ferro-alloys were measured under different conditions and compared. Samples such as Fe - W (W ≃ 80 per cent.), stellite (Co ≃ 50, Cr ≃ 25, W ≃ 20 per cent., the remainder Fe) and ferrovanadium, which are not readily soluble in ordinary acids, can be easily dissolved by the use of a mixture of H_2O_2 and HF (for Fe - V and stellite) or oxalic acid (for Fe - W). These new methods of decomposition can be used for the rapid analysis of iron and steel. K. SAITO

2431. **Rapid methods of solution with hydrogen peroxide. II. Application to the rapid determination of several elements in iron, steel and ferro-alloys.** K. Kawamura (*Japan Analyst*, 1953, **2** [5], 417–421).—The determinations of Si, Mn, P and Cu in iron and steel are not affected by the use of H_2O_2 for a more rapid dissolving of the sample. Chromium steel is decomposed with a mixture of H_2O_2 and HF, treated with $HClO_4$ and titrated, with diphenylamine as indicator. The use of HF rather than H_3PO_4 makes the colour change of the indicator more sensitive. The time taken for a determination of V in vanadium steel or in ferro-vanadium is significantly decreased by dissolving the sample (0·5 to 1 g) in HF (5 to 10 ml) and H_2O_2 (30 per cent.) (20 to 30 ml) and treating with dil. H_2SO_4 (1 + 3) (10 ml). Spiegeleisen (Fe - Mn - Si) (< 150 mesh, 0·5 g) is dissolved in a mixture of H_2O_2 (30 per cent.) (20 ml), conc. HCl (20 ml) and water (40 ml), and treated with conc. $HClO_4$ (20 ml). The silica thus obtained is easily filtered off and ignited. Tungsten in ferrotungsten can be determined by dissolving the sample (< 150 mesh, ≃ 0·5 g) in H_2O_2 (30 per cent.) (20 ml) and water (20 ml) containing oxalic acid (3 g) and pouring the soln. into a mixture of conc. HCl (50 ml), conc. HNO_3 (10 ml) and water (150 ml) to precipitate pure WO_3. The precipitation of WO_3 is completed by the addition of cinchonine, and ignition to WO_3 is effected in the usual way. K. SAITO

2432. **Studies of inorganic and analytical chemistry by the use of ion-exchange resin. VI. Separation of iron and aluminium by a reduction method.** H. Kakihana and S. Kojima (*Japan Analyst*, 1953, **2** [5], 421–426).—The elution of Al^{+++} and Fe^{+++} from a column of Amberlite IR-120 (H) was studied with various eluting agents. Fe^{+++} adsorbed on a column (10 ml of the resin for 1 milli-equiv. of the ion) can be eluted as Fe^{++} with a soln. (500 ml for < 3 milli-equiv. of Fe) containing KI, KCl and HCl (0·1, 0·15 and 0·2 mole per litre, respectively) together with iodine equiv. in amount to the Fe^{+++}. Al^{+++} remain on the column, but can be subsequently eluted with 2 *N* HCl. Both Al and Fe are determined in the eluates. K. SAITO

2433. **The heterometric micro-analysis of cobalt with 1-nitroso-2-naphthol. A general study.** M. Bobtelsky and E. Jungreis (*Anal. Chim. Acta*, 1955, **12** [3], 248–262).—Solutions (20 ml) of Co^{++} (0·2 to 0·5 mg) in 0·05 *M* acetic acid are titrated heterometrically (*Anal. Abstr.*, 1954, **1**, 1212) with ethanolic solutions (≃ 0·01 *M*) of 1-nitroso-2-naphthol (**I**). Other acidic or neutral media can also be used. A 50 per cent. ethanolic medium is more suitable for the lower concn. of Co^{++}; a 0·003 *M* soln. of **I** can then be used and a higher acidity is also permissible. At the end-point, the Co:**I** ratio is 1:4. $Na_3Co(NO_2)_6$ titrated similarly in ethanolic or 50 per cent. acetic acid soln. gives an end-point at a Co:**I** ratio of 1:3. The ppt. yields the same optical density whether pptd. from Co^{++} or $[Co(NO_2)_6]^{'''}$ soln., and the wt. of the dried ppt. obtained from Co^{++} is ≃ 5 per cent. greater than the calculated wt. of (Co + 3**I**). These facts suggest that, in the titration of Co^{++}, 1 mol. proportion of **I** is consumed in oxidising Co^{II} to Co^{III}, and that the same Co^{III} compound is pptd. in both titrations. In 50 per cent. ethanol and in the presence of a large excess of tartrate, the end-point corresponds to a Co:**I** ratio of 1:2. Citrate does not influence these titrations; EDTA prevents the

pptn. of Co^{++} but does not affect the ppt. after its formation. The titration can be used in reverse for the determination of **I**. W. C. JOHNSON

2434. **Heterometric micro-determination of cobalt with 1-nitroso-2-naphthol in the presence of foreign metals.** M. Bobtelsky and E. Jungreis (*Anal. Chim. Acta*, 1955, **12** [3], 263–270).—The methods previously described (*Anal. Abstr.*, 1955, **2**, 2433) are extended to the determination of Co in the presence of Al^{+++}, Cr^{+++}, Pb^{++}, Cd^{++}, Zn^{++}, Ni^{++}, Ba^{++}, Ca^{++} or Mg^{++}. The max. permissible concn. of Ni^{++} is nine times that of the Co^{++}. W. C. JOHNSON

2435. **Studies on spectrophotometry. II. Spectrophotometric determination of a micro-amount of cobalt with nitroso-R salt.** Y. Oka and M. Miyamoto (*Japan Analyst*, 1953, **2** [4], 322–328).—Experimental conditions for the determination of a micro-amount of Co with nitroso-R salt were studied. An excess of reagent in the soln., which shows a marked absorption below 500 mμ (max. absorption of the complex, 415 mμ), can be decomposed by boiling with sodium perborate in HCl soln., whilst the Co complex remains unchanged. Thus the limit of determination was decreased to 0·05 μg per ml. The attempt to decompose the excess of reagent with Br (H. R. Marston *et al.*, *Aust. J. Exp. Biol. Med. Sci.*, 1940, **18**, 343) met with little success, because of the ease with which the decomposition of the Co complex takes place.
K. SAITO

2436. **A rapid photometric determination of cobalt in steel.** S. Hirano and M. Suzuki (*Japan Analyst*, 1953, **2** [4], 316–319).—The application of the colorimetric determination of Co by the use of its thiocyanate complex to a rapid analysis in a factory was studied. The interference of W can be eliminated by the addition of H_3PO_4. No significant interference results from the presence of V and moderate amounts of Ti and Mo. This method permits a rapid analysis (< 20 min.) of Co within the range 0·05 to 5 per cent. *Procedure*—The sample (0·1 g) is treated with 10 ml of mixed acid [H_2SO_4 (1 + 1), 200 ml, H_3PO_4 (85 per cent.), 100 ml, $HClO_4$ (60 per cent.), 60 ml, and water, 140 ml] and HNO_3 (14 *N*) (≃ 3 ml) until white fumes are evolved. The product is made up to 50 ml and a 5-ml portion is treated with liquid cadmium amalgam (≃ 5 ml) to reduce Fe^{+++} to Fe^{++}. Ammonium citrate (210 g of citric acid dissolved in 600 ml of 5 *N* aq. NH_3 and made up to 1 litre with water) (10 ml), NH_4SCN (600 g per litre) (10·0 ml) and ammonium acetate (700 g per litre) (2·0 ml) are added to the aqueous layer, which is extracted with *iso*pentanol - ether mixture (3:1) (10·0 ml). The extinction of the org. solvent layer is measured with a spectrophotometer.
K. SAITO

2437. **Some properties of the green carbonato-cobalt complex and its use for the quantitative analysis of cobalt.** M. Mori and M. Shibata (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [10], 1044–1047).—The formula of green carbonato-Co^{III} complex, which is obtained by the oxidation of Co^{II} salt with H_2O_2 (or preferably with sodium perborate) in the presence of $NaHCO_3$, was determined to be $[Co(CO_3)_3]^{'''}$ by the comparison of its absorption spectrum with trioxalato-Co complex. The attempt to determine a small amount of Co by converting it into this complex and titrating it iodimetrically (Laitinen *et al.*, *Brit. Abstr. C*, 1952, 50), resulted in values too high by 0·7 to 1·5 per cent. In the presence of Fe^{+++}, Cu^{++}, Ni^{++} and Mn^{++} the values were too low by ≃ 1 per cent. The extinction coefficient of this complex at 645 mμ is in accord with Beer's law for 5 to 100 μg of Co per ml. The use of the complex for colorimetric analysis appears more advantageous than Laitinen's method. K. SAITO

2438. **Polarographic determination of nickel in cobalt salts.** J. Doležal and P. Hofmann (*Coll. Czech. Chem. Commun.*, 1955, **20** [1], 151–157).—The polarographic behaviour of cobalt and nickel in a soln. of ethylenediamine tartrate (**I**) and $K_4P_2O_7$ (**II**) is studied and a new method is proposed for the determination of traces of Ni in cobalt salts. To 5 ml of a cobalt salt soln. (≃ 1 *M*), with a pH of about 7, are added 10 ml of a 2 *M* soln. of **II**, 2·5 ml of a 2 *M* soln. of **I** and 0·5 ml of a 0·01 *M* soln. of fuchsine, and the soln. is made up to 20 ml. The blue ppt. formed dissolves on being shaken to give an intense red soln. Nitrogen is blown through this soln. in a polarographic cell before it is polarographed at − 0·8 V (*vs.* the S.C.E.) with a galvanometer sensitivity of ≃ 1:20. A soln. containing 0·5 ml of 0·01 *M* $NiSO_4$ per 20 ml is also polarographed and the concn. of Ni in the test soln. is determined by the standard-addition method. The calibration-curve method can also be used. In the presence of large concn. of Co, traces of Cu and Fe can be determined with an electrolyte containing 0·5 *M* **I** and 0·1 *M* **II**, and traces of Cu and Ni with 0·25 *M* **I** and 1 *M* **II**. It is shown that an electrolyte of **I** and **II** is superior to KSCN, pyridine - HCl, aq. NH_3 soln. - NH_4Cl, KCN or NaF. (This is a translation into Russian of a paper previously published in *Chem. Listy*, 1954, **48**, 1329.) E. HAYES

2439. **Photometric determination of nickel, aluminium and manganese in raw steel.** H. Specker and H. Hartkamp (*Z. anal. Chem.*, 1955, **145** [4], 260–265).—A new photometric method for the determination of small quantities of Ni, Al and Mn in raw steel and iron ore is presented. The steel sample (10 to 100 mg) is dissolved with HCl and HNO_3 in a quartz beaker and, after the addition of a small amount of NaCl, evaporated to dryness. Nitrate is removed by evaporation with HCl, then 2 to 3 ml of conc. HCl are added. The solution is now rinsed into a 200-ml separating funnel, 10 ml of conc. HCl are added and the soln. is diluted with water to 30 ml. Ether and tetrahydrofuran (30 ml of each) are added to the cooled solution, then 15 ml of NH_4SCN solution; the mixture is shaken for 2 to 3 min. and the phases are separated. A second extraction with 20 ml each of ether and tetrahydrofuran and 10 ml of thiocyanate is carried out. Finally, an extraction with 20 ml of ether or chloroform is carried out and the organic phase is rejected. The aqueous phase is adjusted to pH 5·5 to 6 with a buffer solution, treated with 5 ml of dimethylglyoxime (1 per cent., ethanolic) and 10 ml of chloroform and shaken for 2 to 3 min. This operation is repeated, both chloroform extracts are combined and 10 ml of water and 5 ml of bromine water are added. After shaking, making ammoniacal and shaking again, the red extract is made up to 50 ml with water and the colour measured photometrically at 546 mμ. This gives the content of Ni. The nickel-free, buffered solution is treated with 10 ml of 8-hydroxyquinoline (1 per cent., in $CHCl_3$) and extracted with 10 ml of chloroform. The extracts are placed in a 25 to 50-ml calibrated flask and made

up to the mark with chloroform. The extinction of the dissolved Al complex is measured at 405 mμ against pure chloroform. The solution free from Al and Ni is now treated with 10 ml of chloroform and 10 ml of sodium diethyldithiocarbamate soln. (2 per cent., aqueous). After being shaken, the aqueous phase is again extracted with 5 ml of sodium diethyldithiocarbamate soln. and 10 ml of chloroform. The extracts are made up to the mark with chloroform in a calibrated flask and the extinction of the Mn complex is measured at 578 mμ against pure chloroform. The method takes 45 to 60 min.
R. J. MAGEE

2440. **Chelation of platinum group metals. Complexiметric titration of palladium.** W. M. MacNevin and O. H. Kriege (*Anal. Chem.*, 1955, **27** [4], 535–536).—Palladous soln. are titratable complexiметrically by addition of an excess of EDTA (disodium salt) followed by back-titration with $Zn(NO_3)_2$. The pH is controlled at 10 ± 1 by addition of dil. KOH soln. to enable the Eriochrome black T indicator to function properly. Solutions containing 0·6 to 30 mg of Pd are titrated with an accuracy of ± 0·3 per cent. Pt^{II} and Pt^{IV} do not interfere, but Ir and Ru do so at higher concn.; the titration is not applicable in the presence of Rh or Os.
D. R. GLASSON

2441. **Determination of small quantities of iridium.** N. K. Pshenitsyn and I. V. Prokof'eva (*Izv. Sektora Platiny i Drugikh Blagorodnykh Metallov In-ta Obshch. i Neorgan. Khimii Akad. Nauk, SSSR*, 1954, **28**, 229–234; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 50,218).—Solutions of $(NH_4)_2IrCl_6$ are titrated against one of the following reagents: (*i*) 0·01 *N* $(NH_4)_2Fe(SO_4)_2$ in 4 per cent. H_2SO_4 soln., (*ii*) 0·02 *N* $TiCl_3$ in 10 per cent. acetic acid soln., (*iii*) 0·02 *N* quinol soln. containing 20 ml per litre of conc. HCl. Diphenylamine (added close to the end-point) is used as an indicator. All the reagents convert $(NH_4)_2IrCl_6$ into $(NH_4)_2[IrCl_5.H_2O]$. To ensure that no Ir^{III} is present, the soln. to be titrated is treated with chlorine (or other oxidising agent) to convert all the Ir to Ir^{IV}; after the soln. has been set aside for 1 hr. the chlorine is removed by a stream of air. The error with (*i*) is − 1·5 to + 5·2 per cent., with (*ii*) − 6·6 to + 1·9 per cent., and with (*iii*) ± 5·8 per cent. Iridium can be determined colorimetrically by adding an excess of Fe⁺⁺ and *o*-phenanthroline to an acid soln. containing Ir^{IV} and Na acetate to give a pH of 4 and measuring the colour with a green filter. Ammonium fluoride is added to eliminate interference from Fe^{+++}, and blank measurements are made with solutions containing Na acetate, NH_4F and *o*-phenanthroline. The colorimetric results are ≃ 10 per cent. too high.
E. HAYES

2442. **Analytical chemistry in the service of metallurgy.** D. Jentzsch (*Chem. Tech., Berlin*, 1955, **7** [4], 189–194).—In a survey of recent developments in analytical chemistry, examples are given of the use of ion-exchange separation, potentiometric titration, polarography, absorptiometry and other techniques in the determination of both major and minor concentrations of various elements, including particularly Ga, Ge, In and Li. Working details of several methods are provided, together with comparative data on the limits and accuracy of the procedures for certain elements. (19 references.)
J. O. LAY

2443. **Progress in metallurgical analysis.** E. Jaudon (*Chim. Anal.*, 1955, **37** [2], 45–52; [3], 104–111).—A review is given of the applications to metallurgical analysis of modern methods, particularly emission and absorption spectroscopy, electrolytic separation, potentiometry, polarography, chromatography and precipitation and complex-formation with organic reagents. (91 references.)
A. R. ROGERS

2444. **The use of ion-exchange resins in the analysis of coal ash.** P. Ellington and L. Stanley (*Analyst*, 1955, **80**, 313–314).—A rapid wet-oxidation method with H_2SO_4 and HNO_3 for separation of SiO_2 from coal ash has been described (Ellington *et al.*, *Fuel, Lond.*, 1951, **30**, 272). A scheme is now proposed for separation of Fe from the wet-oxidation filtrate and subsequent determination of the other cations present. *Procedure*—The soln. containing the cations in 100 ml of 0·4 *N* H_2SO_4 is run through a column (20 cm × 1 cm) of Amberlite R-120 (H) and the column is washed with 100 ml of water. The eluate containing only H_2SO_4 is discarded. The column is then washed with 100 ml of 3 *N* HCl, the eluate is evaporated to 3 ml, treated with 5 ml of conc. HCl and run through a column (30 cm × 1 cm) of Amberlite IRA-400 (Cl), which is then washed with 40 ml of 8 *N* HCl. Fe is retained on the column. The eluate is evaporated to dryness, dissolved in 20 ml of water and passed through a column of Amberlite IR-120 (H). The column is eluted (*a*) with 0·4 *N* HCl; Na appears in the 200 to 340-ml fraction and K in the 540 to 820-ml fraction; (*b*) with a 5 per cent. citric acid buffer (pH 3); Ti occurs in the first 240 ml and Al in the 600 to 900-ml fraction; (*c*) with *N* HCl; Mg and Ca occur in the 40 to 100-ml fraction and the 360 to 680-ml fraction, respectively. Fe is eluted from the column retaining it with 0·1 *N* HCl. The location of Mn as well as the optimum conditions of these separations are being investigated. The procedure may be applicable to SiO_2-free filtrates in silicate analysis.
A. O. JONES

2445. **Determination of cellulosic constituents in asbestos and asbestos - glass textile materials.** C. Z. Carroll-Porczynski (*J. Text. Inst. Manchr, Trans.*, 1955, **46** [2], T65–70).—A new method of analysis of cellulose in cellulose - asbestos and cellulose - glass fibres mixtures is described. Ignition is carried out at 370° C instead of the normal 800° C, since the wt. of ash of cellulosic fibres ignited at the two temp. is the same, and the loss in weight of asbestos is smaller and more constant at the lower temp. Samples (5 to 10 g) are conditioned at 65 per cent. R.H., 70° F, for 2 hr., weighed, ignited for 1 hr. in an electric furnace at 370° ± 10° C, cooled in a desiccator and weighed. The initial wt. of asbestos or glass is found by dividing the wt. of the ignited sample by 0·975.
L. VALENTINE

See also Abstract 2604.

3.—ORGANIC ANALYSIS

2446. **Determination of organically bound halogen.** I. Simonyi, G. Tokár and G. Gál (*Magyar Kém. Foly.*, 1954, **60** [4], 97–98; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 50,241).—Organic halogen compounds are reduced with Raney nickel catalyst (2 to 3 per cent. of Al) in an alkaline medium, or with Zn and sulphuric acid in the presence of palladised charcoal, the reagent used being dependent on the nature of the compound. The halogen can be determined in ethyl bromide or iodide, chloroform, chloral hydrate, chlorobenzene, *p*-chlorophenol, *p*-chloronitrobenzene, *p*-chloroaniline,

tetra-iodophenolphthalein and phenacyl bromide. The relative error is $\lesssim$ 1 per cent. E. HAYES

2447. **Determination of fluorine in organic fluoro compounds.** C. Eger and A. Yarden (*Bull. Res. Counc. Israel*, 1954, **4** [3], 305–306).—An accurate method applicable to semi-micro quantities (20 to 60 mg) involves: (*a*) transforming the organically bound F into F′ by combustion with Na_2O_2 (Parr bomb) with sucrose as combustion aid and, generally, with $KClO_4$ as an accelerator, and (*b*) passing the solution to be analysed through an acid cation-exchange resin (Amberlite IR-112) to remove Na^+ and then carrying out the determination of F in the usual way by titrating with $Th(NO_3)_4$ soln., with sodium alizarinsulphonate as indicator. The method is applicable to compounds containing also Cl and Br. Representative tabulated results show errors ranging from 0·3 to 0·8 per cent. with nine different fluoro compounds tested in amounts ranging from 3 to 14·5 mg of F′. G. HELMS

2448. **A rapid determination of nitrogen in organic compounds by the iodic acid decomposition method.** S. Ohashi (*Bull. Chem. Soc. Japan*, 1955, **28** [3], 177–181).—If an organic compound containing N is heated with iodic acid in strong phosphoric acid it is decomposed, the N is liberated and can be measured. *Procedure*—Weigh 10 to 50 mg of the substance (producing 1 to 5 ml of N) into a small weighing tube. Previously heat gently in a reaction vessel a mixture of 3 to 5 ml of strong phosphoric acid [pure orthophosphoric acid (d = 1·7) heated to 300° C] and 2 or 3 times the theoretically required weight of KIO_3 until a homogeneous dispersion is obtained. After cooling add the weighing tube and insert a thermometer and a gas-introducing tube into the reaction vessel. Completely displace the air in the apparatus and connect with a nitrometer filled with KOH soln. (30 per cent.). Heat the reaction vessel to a temp. $\gtrsim$ 260° C until no more gas is evolved and no more iodine is liberated. Transfer the gas to the nitrometer with a stream of CO_2. Measure the N and hence calculate the N content of the substance. Satisfactory results were obtained for amines, amino acids, azo compounds, pyrrole, thiazole, etc., but volatile compounds, nitro or nitroso compounds, purines, pyridines, quinolines, etc., did not give good results. The precision and accuracy are not quite so good as with the micro-Dumas or Kjeldahl methods. N. E.

2449. **The determination of oxime nitrogen.** T. Yamada (*Acta Chem. Scand.*, 1955, **9** [2], 349–351).—A method of determining oxime nitrogen by hydrolysis with 2:4-dinitrophenylhydrazine is described. Results with various oximes, *e.g.*, pyruvic oxime, glucosoxime, α-oxoglutaric oxime, acetoxime, are good even in the presence of interfering substances, *e.g.*, pyruvate, α-oxoglutarate, ascorbic acid. Effects of nitrite and hydroxylamine and methods of eliminating them are given. O. M. WHITTON

2450. **The micro-determination of phosphorus in organic compounds.** J. D. Burton and J. P. Riley (*Analyst*, 1955, **80**, 391–395).—A rapid and accurate procedure for the micro-determination of P in a variety of organic compounds is described, the compound being decomposed by Na_2O_2 in a Parr bomb and the resulting PO_4''' determined spectrophotometrically. *Procedure*—The sample ($\equiv$ 0·1 to 0·25 mg of P) is placed in a Parr micro-bomb with 0·05 g of a mixture of KNO_3 with sugar or mannitol (3 + 1) which has been previously intimately mixed with 0·25 g of Na_2O_2. The bomb, held in tongs, is heated in a micro-burner for 1 min. after detonation has been felt. The contents are rinsed with hot water into 9 ml of 2 per cent. v/v H_2SO_4, and heated on the water bath with a piece of platinum foil electroplated with platinum black to promote decomposition of H_2O_2. The liquid is made just alkaline to phenolphthalein with *N* NaOH and then just acid with 1 drop of 2 per cent. H_2SO_4. The filtered soln. is adjusted to 100 ml and 10-, 15- or 20-ml portions are placed in 25-ml calibrated flasks. To each portion are added 0·75 ml of 10 per cent. H_2SO_4 and 1 ml of ammonium molybdate reagent (1·3 g per 100 ml). After 5 min., 2·5 ml of Metol - sulphite reagent (2·5 g of *p*-methylaminophenol sulphate dissolved in a soln. of 10 g of $Na_2SO_3.7H_2O$ in 400 ml of water, treated with another 40 g of sulphite and diluted to 500 ml) are added and the mixture is diluted to 25 ml. After 1·5 hr. the optical density is measured in a 1-cm cell at 820 mμ and corrected for that of a reagent blank prepared in the same way with omission of the sample. The calibration graph is prepared by development of the colour with known amounts of KH_2PO_4 soln. ($\equiv$ 10 mg of P per litre) in the presence of the appropriate amount of Na_2SO_4 to compensate for that derived from the Na_2O_2. Alternatively, Na_2SO_4 may be omitted in the construction of the calibration graph and correction factors (quoted) may be applied to the observed optical density of the sample soln. after deduction of the blank. Arsenate, germanate and silicate interfere by yielding molybdenum blue. Calibrated and other flasks used in the method should be treated overnight with conc. H_2SO_4 and HNO_3 (1 + 1), washed and not allowed to dry before use to prevent solution of SiO_2. The *N* NaOH used should be stored in a polythene bottle. With compounds containing C–P links the amounts of nitrate - sugar mixture and Na_2O_2 used in the initial fusion should be three times those stated. A. O. JONES

2451. **Diethylammonium diethyldithiocarbamate for the separation and determination of small amounts of metals. II. The isolation and determination of arsenic, antimony and tin in organic compounds.** P. F. Wyatt (*Analyst*, 1955, **80**, 368–379).—Of the compounds formed by reaction of an organic base (*e.g.*, diethylamine, dibenzylamine or piperidine) with CS_2, which serve as complexing agents with a high solubility in extracting solvents, diethylammonium diethyldithiocarbamate (**I**) proved most suitable for separation of As···, Sb··· and Sn·· in mineral acid soln. by formation of complexes extractable by $CHCl_3$. The extracted complex is readily decomposed for determination of the three elements. After examination of the limited number of good methods for subsequent determinations, the following are recommended—(*a*) micro-titration of As··· with $KBrO_3$ with 7:8-benzoflavone as indicator, or absorptiometric determination by reduction of molybdoarsenate to molybdenum blue by hydrazine sulphate; (*b*) micro-titration of Sb··· with $KBrO_3$ as for As, or absorptiometric determination as iodoantimonite, or extraction of $SbCl_5$ into *iso*propyl ether and absorptiometric determination by means of rhodamine B; (*c*) determination of Sn by reaction of Sn^{IV} with 8-hydroxyquinoline in HCl soln. buffered with sodium acetate, and extraction and absorptiometric determination in $CHCl_3$, or turbidimetric determination by means of 4-hydroxy-3-nitrophenylarsonic

acid. Procedures for the isolation of the elements by extraction with a soln. of **I** in $CHCl_3$ and for the decomposition of the extract and for the accurate determination of the three metals by these methods are given. Cu and Bi interfere, but can be removed by means of the same reagent before reduction of the As, Sb and Sn to their lower valency states, since As^{V}, Sb^{V} and Sn^{IV} do not form complexes with **I**. A. O. JONES

2452. **Chromatographic determination of carboxyl groups in filter-paper.** A. J. Ultee, jun., and J. Hartel (*Anal. Chem.*, 1955, **27** [4], 557–560).—A chromatographic method for determining the carboxyl groups in filter-paper is presented. The paper is treated with a small aliquot of lead nitrate or acetate soln., 0·01 to 0·1 *M* according to the type of paper to be analysed; the Pb forms a strong bond with the carboxyl groups of the paper. The paper is suspended in boiled distilled water, which is allowed to rise up the paper to at least 10 cm, and the lead spot is made visible by H_2S. The area of the spot is measured and then cut out and weighed, the carboxyl content being calculated from this and the wt. per sq. cm of the untreated paper. G. P. COOK

2453. **Colorimetric determination of the perchlorate ion in organic perchlorates.** W. Bodenheimer and H. Weiler (*Bull. Res. Counc. Israel*, 1954, **4** [3], 316).—The method is based on the decrease in colour intensity of the highly coloured complex cupric tetrapyridine ion when the perchlorate derivative is pptd. A calibration curve is first obtained as follows. Quantities ranging from 0·3 to 4·0 mg of $KClO_4$ are added to 5-ml quantities of a standard aq. solution containing 4·883 g of $Cu(NO_3)_2.3H_2O$ and 100 ml of pyridine per litre. Each test solution is saturated with NaCl, which reduces the solubility of the cupric tetrapyridine perchlorate (**I**), thereby enhancing the sensitivity of the method. After a few hours, the blue crystalline scum of **I** is filtered off and the optical density of the filtrate is determined in a Klett-Summerson colorimeter with filter No. 66 (transmission range $\simeq$ 640 to 700 mμ). The measured optical densities are then plotted against the amount of perchlorate ion taken. The determination of unknown perchlorate content in an organic perchlorate is made by adding a weighed quantity to 5 ml of the standard soln., saturating with NaCl, measuring the optical density of the filtrate and reading off the perchlorate content from the calibration curve. Illustrative data are given for 7 organic perchlorates. G. HELMS

2454. **Method and apparatus for the colorimetric determination of small quantities of acetylene.** G. Almásy and I. Pallai (*Magyar Kém. Foly.*, 1953, **59** [7], 200–203; *Referativnŷĭ Zh., Khim.*, 1954, Abstr. No. 50,243).—In the colorimetric determination of acetylene by means of $Cu(NO_3)_2$, the operations of sampling, precipitation, filtering off, washing and solution of the ppt. are all carried out in the same vessel. The error is $\pm$ 0·05 per cent. E. HAYES

2455. **Study of the composition of hydrocarbon mixtures with the mass spectrometer.** W. Żuk (*Ann. Univ. M. Curie-Skłodowska*, 1953, **8** [6], 1–13; *Referativnŷĭ Zh., Khim.*, 1954, Abstr. No. 50,194).—The qualitative determination of hydrocarbons of mass number $\not>$ 60 in gas oil is described. The spectrum of dry gas oil comprises groups of maxima, corresponding to the mass numbers 12 to 16, 24 to 30 and 37 to 44, and the unresolved group 57 to 59. The spectrum indicates the presence in the mixture of propane, *n*- and *iso*-butane, methane and traces of ethane; N and O are not present. The hydrocarbons are not appreciably absorbed on the walls of the ion source. The presence of H_2O in gases leads to the appearance of the residual H_2O spectrum. E. HAYES

2456. **Quantitative determination of ethylene oxide in gaseous mixtures.** V. A. Pokrovskiĭ and G. P. Alishina (*Zavod. Lab.*, 1955, **21** [4], 415–416).—An absorption apparatus not involving the use of mercury, which causes errors when large amounts of carbon dioxide are present, is described for the determination of ethylene oxide in gases. G. S. SMITH

2457. **Quantitative determination of ethylene oxide adducts in their aqueous solutions or dispersions.** N. Schönfeldt (*J. Amer. Oil Chem. Soc.*, 1955, **32** [2], 77–79).—A method is described for the quant. determination of ethylene oxide adducts based upon the reaction between these adducts and ferrocyanic acid. The reaction takes place on the ethylene oxide chain, one mole of ferrocyanic acid being required to ppt. an adduct containing 6 units of ethylene oxide. The adduct is pptd. in HCl solution with a known quantity of $H_4Fe(CN)_6$, and after filtration the excess of $H_4Fe(CN)_6$ is determined by titration with standard $ZnSO_4$ solution. D. BAILEY

2458. **Infra-red spectra of alkyl hydroperoxides.** H. R. Williams and H. S. Mosher (*Anal. Chem.*, 1955, **27** [4], 517–521).—The i.r. spectra of seventeen primary and secondary alkyl hydroperoxides were recorded between 2 and 15 μ and are illustrated. In each case the hydroperoxide showed a weak but characteristic absorption in the 11·4 to 11·8-μ region, but several of the corresponding alcohols also absorbed in this region and it was therefore not a unique means of characterising the hydroperoxide. All primary and secondary alkyl hydroperoxides showed absorption in the 12·0 to 12·5-μ region, normal alkyl hydroperoxides having an even number of C atoms showed two max. at $\simeq$ 12·1 and 12·4 μ, and those having an odd no. of C atoms gave a single max. at $\simeq$ 12·3 μ. G. P. COOK

2459. **Determination of trimethylene glycol in crude glycerin.** W. Lazarus and T. H. Newlove (*Analyst*, 1955, **80**, 276–279).—The new method described is based on the non-reaction of trimethylene glycol with $NaIO_4$ under the test conditions and the determination of water in glycerin by the Karl Fischer method. The glycerin (100 g), in a distillation flask fitted with a rubber stopper carrying a thermometer and a capillary air-inlet tube, is distilled under reduced pressure (15 to 30 mm) into a tared receiver. When the temp. corresponding to the b.p. of the glycerin under the partial pressure attained (190° C at 30 mm) has been reached, distillation is continued until about 30 per cent. of the sample has been distilled. The distillate containing glycerol, water and all the trimethylene glycol is weighed and then transferred to a dry bottle fitted with a ground-glass stopper. The glycerol is determined by the $NaIO_4$ method (Erskine *et al.*, *Anal. Abstr.*, 1954, **1**, 498) and water by the Karl Fischer method (B.S. 2511:1954). The trimethylene glycol content of the distillate is ascertained by difference and that of the original sample by calculation. With distilled glycerin the

distillation step is omitted. As in earlier methods, other compounds of similar volatility present in crude glycerin will be determined as trimethylene glycol. A. O. JONES

2460. **Separation of some lower fatty acids by chromatography.** C. Bighi and G. Trabanelli (*Ann. Chim., Roma*, 1955, **45** [2–3], 109–114).—Ascending and descending paper chromatography is used to separate mixtures of lactic acid with glycollic, malic, succinic, citric and oxalic acids, which occur in technical lactic acid obtained as a by-product in the sugar industry. The problem of the preponderance of lactic acid is overcome by using as solvent a mixture of *iso*propanol, *tert.*-butanol, benzyl alcohol and water (1:1:3:1), with 2 per cent. of formic acid (90 per cent.). Values of R_F and limits of separation are given and discussed. C. A. FINCH

2461. **Separation of some lower fatty acids from lactic acid by chromatography.** C. Bighi and G. Trabanelli (*Ann. Chim., Roma*, 1955, **45** [2–3], 115–122).—The Lugg - Overell method is employed for the chromatographic separation of succinic, glycollic, malic, citric and oxalic acids from technical lactic acid obtained by the fermentation of sugar by-products. The concn. limits at which these acids may be identified with certainty are determined as 1 pt. of the acids named in 40 pt. of lactic acid. C. A. FINCH

2462. **Utilisation of ion exchangers in analytical chemistry. XXIX. Sorption and elution of some low-molecular-weight organic acids.** S. Berntsson and O. Samuelson (*Acta Chem. Scand.*, 1955, **9** [2], 277–282).—The sorption and elution of glycollic, oxalic, pyruvic, gluconic, maleic and toluene-*p*-sulphonic acids by means of the strongly basic resin Dowex 2 (acetate form) and the weakly basic resin Dowex 3 (free-base form) have been studied. All acids except gluconic can be taken up quantitatively by the resins. Glycollic, oxalic, gluconic and maleic acids can be quantitatively displaced from both types of resin by means of 0·5 *M* H_2SO_4 or 0·5 *M* $(NH_4)_2CO_3$ soln. From the strongly basic resin, pyruvic acid can be displaced quantitatively only by means of acid eluents. The elution of this acid from the weakly basic resin is in no case quantitative. Hydrochloric acid is the most effective eluent for toluene-*p*-sulphonic acid from the strongly basic resin, whereas the weakly basic resin is most easily regenerated with sodium hydroxide. O. M. WHITTON

2463. **Electrophoretic separation of sugars and their derivatives.** B. Galos and W. Ostrowski (*Bull. Acad. Sci. Polon.*, 1954, **2**, 61–65).—The separation was effected on strips of No. 4 Whatman paper, using a buffer of boric acid (0·05 *M*), KCl (0·05 *M*) and NaOH (0·012 *M*) at pH 8·6. A drop of creatinine solution was placed on a paper strip parallel with a drop of sugar solution; the creatinine did not migrate in the electric field but advanced by electro-osmotic forces only. The time for electrophoresis was 8 hr., the voltage was 195 V, the tension 15 mA and the temp. 21° C. Aniline phthalate was used as spraying reagent. The mobility of the sugars was calculated by the formula

$$u = Sa + Sb\Big/\frac{Et}{l}$$

where u = mobility, Sa = the path taken by the sugar, Sb = the path taken by creatinine, E = voltage, l = length of paper strip in cm, t = time in sec. The results show that most pentoses and hexoses migrate more quickly than oligosaccharides, but melibiose migrated more quickly than methylpentose rhamnose, and raffinose than cellobiose or sucrose. Ketoses migrate more quickly than aldoses because they react with borate more easily. Mobility was affected by temp., the optimum being 19° to 21° C; below 16° C or above 23° C the mobility was diminished. Glucosamine, in contrast to all the other sugars tested, migrated towards the cathode. SUGAR IND. ABSTR.

2464. **Use of furanosides in separations of carbohydrates on charcoal columns.** S. A. Barker, E. J. Bourne and D. M. O'Mant (*Chem. & Ind.*, 1955, [16], 425).—Mild treatment with methanolic HCl followed by chromatographic fractionation on charcoal offers a general method of wide scope for fractionating mixtures of oligosaccharides. A mixture of nigerose and maltose was resolved by treating 4 g with 180 ml of 4 per cent. methanolic HCl at room temp. until the $[\alpha]_D^{17}$ showed no further change (73 min.); the soln. was neutralised with Ag_2CO_3, centrifuged and concentrated at 35° C *in vacuo* over freshly washed and dried $BaCO_3$. A filtered soln. of the resulting syrup was placed on a column (17 cm × 4·7 cm²) prepared from charcoal which had been washed with water until free from acid and then dialysed for 3 weeks against running water. Elution with 5 per cent. ethanol yielded maltose as the only component. Elution with 10 per cent. and with 30 per cent. ethanol yielded fractions identified as methyl furanosides of nigerose. Similar procedures were used to separate the two trisaccharides produced by partial hydrolysis of nigeran, and also to separate cellobiose and laminaribiose. H. F. W. KIRKPATRICK

2465. **Determination of methylpentoses.** M. N. Gibbons (*Analyst*, 1955, **80**, 268–276).—The colorimetric method of Dische *et al.* (*Brit. Abstr. C*, 1949, 1322) for the determination of methylpentoses has been modified by substitution of thioglycollic acid for cysteine hydrochloride. *Procedure*—The methylpentose soln. (1 ml containing 10 to 40 μg) in a test-tube cooled in ice is treated slowly with 4·5 ml of dil. H_2SO_4 (6 + 1), shaken thoroughly, warmed to room temp. and, together with a standard soln. of a methylpentose (*e.g.*, fucose) and a reagent blank, is placed in a bath of vigorously boiling water for 10 min. Sealed ampoules, containing ≃ 1 ml of water, placed in the necks of the tubes act as condensers. The tubes are cooled and 0·1 ml of aq. thioglycollic acid (3·3 per cent. v/v) is added to each and the tubes are set aside in the dark for 3 hr. The difference between the absorbancies at 400 and 430 mμ is measured for each soln., and the wt. of methylpentose present is calculated by comparison of the result with that of the known wt. in the standard tube. Use of thioglycollic acid improves the accuracy of the method. The behaviour of a number of possible interfering substances has been investigated. A. O. JONES

2466. **Method of assay for ethyleneimine derivatives.** E. Allen and W. Seaman (*Anal. Chem.*, 1955, **27** [4], 540–543).—To an accurately weighed quantity of the sample (≃ 3 mg) add 50 ml of 20 per cent. $Na_2S_2O_3.5H_2O$ soln. and 1 drop of methyl orange. Titrate immediately with 0·1 *N* HCl until the end-point colour persists for > 10 sec. and set aside for 30 min. Add phenolphthalein and titrate with 0·1 *N* NaOH. Run a blank on 50 ml of the $Na_2S_2O_3$

soln. in the same manner. The acid consumption minus the consumption of alkali, corrected for the blank, is equivalent to the ethyleneimino groups present. Assay of 9 ethyleneimine derivatives gave a standard deviation of $\simeq \pm 0{\cdot}1$ per cent.

G. P. Cook

2467. **Determination of carboxylic amides by reduction to the corresponding amine.** S. Siggia and C. R. Stahl (*Anal. Chem.*, 1955, **27** [4], 550–552).—The method is based on the reduction of primary, secondary and tertiary amides to the corresponding amine with lithium aluminium hydride. The resulting amine is steam-distilled from the reaction mixture and is titrated with standard acid. Application to 22 amides, extending from those of low molecular wt. to higher fatty compounds, was satisfactory. The accuracy and precision are usually better than $\pm$ 2 per cent. Other types of amides can be determined by the procedure.

G. P. Cook

2468. **Volumetric determination of nitrocellulose and nitroguanidine by transnitration of salicylic acid.** H. Stalcup and R. W. Williams (*Anal. Chem.*, 1955, **27** [4], 543–546).—Nitrogen in nitrocellulose samples and nitramine nitrogen in nitroguanidine are determined volumetrically by the transnitration of salicylic acid in H_2SO_4 soln., the sample acting as the nitrating agent; the resulting nitrosalicylic acid is reduced with standard $TiCl_3$, the excess being determined by standard ferrous ammonium sulphate soln. with NH_4SCN as indicator. Results were in good agreement with nitrometer values, and a standard deviation of $\pm$ 0·02 per cent. was obtained on standard samples.

G. P. Cook

2469. **Comparative investigation of some methods for the determination of the nitrogen content of nitrocellulose.** P. Verschragen (*Anal. Chim. Acta*, 1955, **12** [3], 227–230).—Five commonly used methods for the determination of N in nitrocellulose have been compared, with particular regard to the reproducibility of results. The preferred method is that of Schlösing (Kast and Metz, "*Chemische Untersuchung der Spreng- und Zünd-stoffe*," Braunschweig, 1931, p. 217).

W. C. Johnson

2470. **Spectrophotometric determination of aliphatic sulphides.** S. H. Hastings and B. H. Johnson (*Anal. Chem.*, 1955, **27** [4], 564–565).—The method of Hastings (*Brit. Abstr. C*, 1953, 350), in which the u.v. absorption spectrum of the complex formed by aliphatic sulphides with molecular iodine is measured, is modified. Improved accuracy and precision are attained by (*i*) maintaining strict temp. control or applying a temp. correction, (*ii*) providing a large excess of iodine over the sulphide concn. ($\simeq$ 81 times) and (*iii*) in samples having a low sulphide concn. removing the sulphides from a portion of the sample by treatment with $HgNO_3$ and using this soln. as a blank.

G. P. Cook

2471. **Potentiometric determination of xanthates.** M. Oktawiec (*Prace Inst. Minist. Hutnic.*, 1954, **6** [4], 184–187).—Contaminated xanthates are determined potentiometrically with 0·05 *M* $Cu(NO_3)_2$ solution (titre established electrolytically) in the presence of an indicator copper electrode, after elimination of impurities (S'' and CS_3'' ions) with a freshly prepared suspension of $ZnCO_3$ and a 20 per cent. $BaCl_2$ solution. The suspension of $ZnCO_3$ is prepared by mixing a solution of 20 g of $NaHCO_3$ in 180 ml of H_2O with a solution of 1 g of $ZnSO_4$ in 200 ml of H_2O, filtering off the resulting amorphous ppt. without suction and diluting it to 500 ml. A known amount of this suspension is added to the test substance (containing 0·2 to 0·3 g of xanthate) 2 to 3 hr. before titration, followed by addition of a known amount of $BaCl_2$ solution 15 min. before titration. The filtrate from this mixture (obtained without suction) is diluted to 200 ml. After immersion of a calomel electrode and an indicator electrode (a thin sheet of copper, pretreated by control determination of pure xanthate, special cleaning and storage in water) the titration is carried out, with stirring. Comparison of this method with the usual potentiometric, alkalimetric and iodimetric determinations of pure K ethylxanthate proved its accuracy within $\pm$ 0·5 per cent.

S.C.I. Abstr.

2472. **Infra-red spectra of naphthalene monosubstitution compounds.** H. Kamada and Y. Nishino (*Japan Analyst*, 1953, **2** [4], 338–342).—Infra-red spectra (11 to 14 μ) of 11 substitution compounds (both 1- and 2-) of naphthalene, including those of benzyl-, benzoyl-, acetyl-, chloro-, methyl- and nitro-naphthalenes, were observed in CS_2 soln. (0·3 *M*, thickness of layer 0·1 mm) and their mutual relationship is discussed. Specific extinction coefficients of some of them were measured and the possible use of the absorption spectra for chemical analysis is discussed. For this, the integral method appears to be more advantageous than the ordinary max. absorption method.

K. Saito

2473. **Use of Gibbs' reagent for the analysis of phenol mixtures.** M. Bohdanecký (*Chem. Průmysl*, 1954, **4** [1], 25–26; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 50,252).—The determination of small quantities of phenols in solutions of *p*-cresol (**I**), *p-tert.*-butylphenol (**II**), salicylic acid (**III**) and *p*-hydroxybenzoic acid (**IV**) is based on their reaction with 2:6-dibromoquinonechloroimine (**V**) to form a blue colour. **I**, **II**, **III** and **IV** do not react with **V**. 2:6-Dichloroquinonechloroimine (**VI**) can be used instead of **V**. One ml of a soln. of **VI** (8 mg in 2 ml of 95 per cent. ethanol and diluted to 25 ml) and 2 ml of a borate buffer soln. (pH 9·6) are added to 2 ml of the test soln. ($\gtrsim$ 10 μg of phenol per ml), and the colour is measured after 45 min. in a Pulfrich photometer with filter S53, S57, S61 or S66. The relative error is 2·5 per cent. The reagent soln. is stable for $\gtrsim$ 2 days in the cold.

E. Hayes

2474. **Colorimetric estimation of *p*-hydroxybenzoic acid and its esters.** J. Deshusses (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [1], 37–40).—The colorimetric reagent prepared from *p*-nitroaniline (**I**) (Duncan and Dustman, *Ind. Eng. Chem., Anal.*, 1938, **9**, 416) is preferred to the gravimetric procedure and as an alternative to Millon's reagent for the determination of *p*-hydroxybenzoic acid (**II**) and its esters in fruit juices. Addition of weighed amounts of **II** to apple juice and grape juice gave 89 to 100 per cent. recovery by this means. *Reagent*—To 9 ml of a soln. of **I** [made by dissolving 3·5 g of **I** in water (5 ml) and 37 per cent. HCl (45 ml) and diluting to 500 ml], add 9 ml of 5 per cent. $NaNO_2$ soln. Cool in ice for 5 min. and add 36 ml of 5 per cent. $NaNO_2$ soln. Dilute to 100 ml and cool for 15 min. in ice. *Reference curve*—Prepare standards containing 5, 10, 15 and 20 ml of a soln. of **II** (100 mg of **II** in 2 ml of *N* NaOH diluted and carefully acidified with *N* H_2SO_4, neutralising the excess of acid with $NaHCO_3$, and diluting to 500 ml). Mix each quantity with 20 ml of 4 per cent.

borax soln., 400 ml of water and 10 ml of reagent. Mix, set aside for 15 min., then dilute to 500 ml. A Pulfrich photometer with filter S47 gives satisfactory readings. *Procedure*—Extract a quantity of the fruit juice 3 times with an equal quantity of ether; carefully distil off the ether, removing the last 2 to 3 ml with dry air. Dissolve the residue in 10 ml of 96 per cent. ethanol and purify it by passing it through a column (14 cm × 1 cm) of chromatographic alumina (Brockmann), washing 4 times with 10-ml portions of ethanol. Evaporate the ethanol to 2 ml and saponify the residue by boiling under reflux with *N* NaOH (10 ml) for 2 hr. Cool, and neutralise with *N* H_2SO_4, continuing as described above for the preparation of standards, using an appropriate aliquot if necessary.
D. G. FORBES

2475. **Quantitative determination of *tert.*-butyldimethylacetophenone and musk ketone.** K. A. Bogdanov (*Maslob.-Zhir. Prom-st'*, 1953, [8], 18–19; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 46,889).—4-*tert.*-Butyl-2 : 6-dimethylacetophenone (**I**) and 4-*tert.*-butyl-2 : 6-dimethyl-3 : 5-dinitroacetophenone (**II**) (musk ketone) are determined gravimetrically in the form of their condensation products with anisaldehyde. *Procedure*—To a weighed sample of ketone (≃ 1 g) in a 50-ml beaker add 10 to 15 ml of a 10 per cent. ethanolic soln. of anisaldehyde and dissolve by gentle heat. Add 3 or 4 drops of a 40 per cent. aq. soln. of NaOH and boil for 1 to 2 min. Collect the crystals formed on a glass filter, wash with 50 per cent. ethanol until the washings are neutral to phenolphthalein, and dry to constant weight at 60° to 70° C. Calculate the amount of ketone by multiplying the wt. of crystals by 0·6335 for **I**, and by 0·7135 for **II**. **I** forms greenish yellow crystals with m.p. 128° to 129° C and **II** forms silky greenish yellow acicular crystals with m.p. 167° to 168° C. The error is ± 2 per cent.
E. HAYES

2476. **Quantitative analysis by infra-red spectroscopy. III. Determination of isomers of *cyclo*hexyldinitrophenol.** H. Kamada and S. Tanaka (*Japan Analyst*, 1953, **2** [4], 334–338).—The quantitative analysis of 4-*cyclo*hexyl-2 : 6-dinitrophenol (**I**), an isomer of 6-*cyclo*hexyl-2 : 4-dinitrophenol (**II**) (agricultural chemical), was studied with the aid of i.r. spectroscopy. The i.r. absorption spectra of these two compounds are so similar (max. absorption, **II**, 10·98 μ; **I**, 10·89 μ) that the usual extinction method with two key bands cannot be applied. When the extinctions of the sample soln. (≃ 15 mg per ml, in CS_2) are measured at several wavelengths (key bands), including 9·31, 10·78, 10·89, 11·01 and 14·06 μ, and the "normal equation" is solved by the method of least squares, both isomers can be determined in the mixture (up to 40 per cent. of **I** in **II**) with an average deviation of ≃ 0·6 per cent. from the mean. When the approx. composition of the sample is known, the compensation method can also be applied by the use of standard soln. containing approx. the same amounts of **II** as the sample soln.
K. SAITO

2477. **Polarography of aromatic heterocyclic compounds. I. Oscillographic differentiation of some pyridine derivatives.** J. Volke and V. Volková (*Chem. Listy*, 1954, **48** [7], 1031–1038).—Oscillographic polarography with an electronic polaroscope and a streaming- or dropping-mercury electrode overcomes to a large extent the failure of normal polarographic methods to determine two different reducible pyridine derivatives in the presence of each other. A comparison of the oscillographic curves of nicotinic, picolinic, *iso*nicotinic, dipicolinic, dinicotinic and *iso*cinchomeronic acids, and those of nicotinamide, trigonelline, nicotine and isoniazid makes it possible to differentiate between the individual compounds in a mixture, consisting in favourable cases of as many as five components.
G. GLASER

2478. **Testing of mineral-oil hydrocarbons: the determination of the total sulphur content by using Sandlar's sulphur lamp.** German Standard DIN 51,771 (*Erdöl u. Kohle*, 1955, **8** [3], 178–180).—With the aid of Sandlar's sulphur lamp, the gaseous or liquid sample is burnt in a stream of O and the oxides of S thus formed are quantitatively converted into H_2SO_4 by means of conc. H_2O_2. The H_2SO_4 is determined volumetrically by titration with standard NaOH (methyl red - methylene blue), or gravimetrically by pptn. with $BaCl_2$ soln. The apparatus is described fully with the aid of diagrams, and details of the analytical procedure are given.
C. J. KEATTCH

2479. **Further observations on the determination of elementary sulphur in petrol by Sommer's test.** G. E. Mapstone (*Erdöl u. Kohle*, 1955, **8** [3], 174–175).—Further observations are made on Sommer's test for the determination of elementary sulphur in petrol, with special reference to an article by Albert (*Anal. Abstr.*, 1954, **1**, 3029).
C. J. KEATTCH

2480. **Spectrophotometric determination of aliphatic sulphides in crude petroleum oils and their chromatographic fractions.** H. V. Drushel and J. F. Miller (*Anal. Chem.*, 1955, **27** [4], 495–501).—A modification of an earlier procedure by Hastings (*Brit. Abstr. C*, 1953, 350, and *Anal. Abstr.*, 1955, **2**, 2470) permits the determination of aliphatic sulphides in small samples of high-mol.-wt. material such as a crude-oil chromatographic fraction. The higher iodine concn. used in the formation of intermolecular sulphide - iodine complexes (of absorption max. 308 mμ) increase the sensitivity, so that by using a Beckman DU spectrophotometer with photomultiplier attachment smaller samples may be determined, substantially reducing the sample absorption in the u.v. region; samples containing high concn. of aromatic hydrocarbons are thus analysed. Interference from hydrocarbon - iodine complexes is negligible. An overall accuracy of ≃ 10 per cent. is estimated for the method, which should be valuable in characterisation of crude petroleum before refinery operations.
D. R. GLASSON

2481. **Determination of the "sulphated ash" on lubricating greases.** German Standard DIN 51,803 (*Erdöl u. Kohle*, 1955, **8** [3], 176–177).—The determination of the "sulphated ash," instead of the unreliable "oxide ash," is adopted. The "sulphated ash" is defined as the residue obtained on ignition of the ash with H_2SO_4. Its determination can be used in estimating the purity of the sample and also enables conclusions to be drawn as to the kind of saponifying medium present and on the existence of a filler. With lead soaps the temp. of the furnace must not exceed 700° C, since Pb is lost. In the presence of large amounts of Zn, the determination can be carried out without the risk of ZnO formation. The procedure is applicable to non-graphic, alkali, alkaline-earth, and mixed alkali - alkaline-earth greases. The error is ± 5 per cent.
C. J. KEATTCH

2482. **Infra-red spectrometer in analysis of mineral oils and greases.** L. Roberts and J. Favre (*Rev. Inst. Franç. Pétrole*, 1955, **10** [3], 164–169).—Absorption spectra of mineral oils and their heavier fractions in the region 7 to 15 μ show bands characteristic of paraffins and alkylaromatics observed in medicinal paraffin, pine-resin oil, and polymer oils from alkyl-benzenes and -naphthalenes. The spectra will also show the presence in lubricating oils of additives, etc. (polyesters, dithiophosphates, trialkylphenol, Na soap, oleate).

A. R. PEARSON

2483. **Determination of moisture in crude tar oils by the Karl Fischer titration method.** T. Ozaki (*Japan Analyst*, 1955, **4** [1], 11–14).—A determination of moisture in crude tar by the Karl Fischer method with the aid of a dead-stop electro-titrimeter is proposed. Toluene of known water content is the best solvent. The sample (water content $<$ 15 per cent.) is dissolved in $\simeq$ 10 times its weight of toluene (water content $\simeq$ 0·2 mg per ml) and submitted to the Karl Fischer titration. The velocity of titration must be slightly lower than usual, because of the slower response of the apparatus. This method compares favourably with the conventional distillation method.

K. SAITO

2484. **Determination of acetovanillone in oxidised alkaline-cleaved sulphite liquor by paper chromatography.** E. T. Reaville and G. W. Shreve (*Anal. Chem.*, 1955, **27** [4], 565–566).—To a strip of Whatman No. 1 filter-paper are added $\simeq$ 60 mg of the liquor sample at about 2 in. from one end. The sample is acidified by holding the paper strip over boiling glacial acetic acid for a few min., and approximately 0·1 ml of warm 41 per cent. sodium metabisulphite soln. is added in a band about 0·5 in. wide just above the sample. The bisulphite band is dried and is placed over water in a closed container for 30 min. The strip is then placed in *n*-butyl ether and the chromatogram developed for $\simeq$ 2 hr. After development, the paper is dried and the acetovanillone detected by u.v. light and by spraying with 2:4-dinitrophenylhydrazine. The band is cut out and is leached from the paper with 10 ml of a phosphate buffer at pH 7·3. Spectrophotometric measurement is then made at 400, 360, 337·5, 320 and 275 mμ with a buffer soln., prepared by treatment of the filter-paper as a blank, in the reference cell. The acetovanillone content is calculated from these measurements, which also correct for interference by a yellow compound, probably vanillil. The accuracy is $<\pm$ 5 per cent.

G. P. COOK

2485. **Determination of labile sulphur in photographic gelatin.** L. Švestka (*Přehl. Fotogr. a Filmové Techn.*, 1953, **6** [5–6], 81–84; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 46,865).—The following methods for the determination of organically combined S in gelatin are compared: (*i*) Sheppard and Hudson (*Ind. Eng. Chem., Anal.*, 1930, **4**, 73–75), (*ii*) Steigmann (*Sci. Ind. Photogr.*, 1949, **20**, 318–319), (*iii*) Abribat (*Sci. Ind. Photogr.*, 1941, **12**, 1). The third is the most accurate; this is based on reaction of the labile S with ammoniacal soln. of $AgNO_3$ to form Ag_2S, and potentiometric determination of the excess of $AgNO_3$ with thiourea or allylthiourea soln., an Ag_2S electrode being used. The method is applied to a study of the kinetics of sulphur cleavage in the hydrolytic decomposition of gelatin.

E. HAYES

2486. **Rapid method for the volumetric determination of antimony, copper or iron in textile materials.** A. G. Hamlin (*J. Text. Inst. Manchr, Trans.*, 1955, **46**, T247–255).—See *Anal. Abstr.*, 1955, **2**, 325.

2487. **Rapid method for the determination of copper, chromium, aluminium and iron in impregnated fabrics.** Z. K. Yakubenko (*Tekstil'naya Prom-st'*, 1954, [5], 32–36; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 50,206).—A sample of fabric (3 to 5 g) is ashed, the ash is moistened with 10 to 12 ml of 30 per cent. H_2O_2 soln. and treated with 8 to 12 ml of conc. H_2SO_4. After Cu and Fe have been separated from Cr and Al, Cr^{III} is oxidised to Cr^{VI} with H_2O_2 in NaOH soln. Copper is separated from Fe with aq. NH_3 soln., Cr^{VI}, Cu^{II} and Fe^{III} are determined iodimetrically; Al is pptd. with 8-hydroxyquinoline, the ppt. is acidified and treated with excess of KBr - $KBrO_3$ soln., and the excess is determined iodimetrically.

E. HAYES

2488. **Determination of xylan in jute.** W. G. Macmillan, A. B. S. Gupta and A. S. Dutt (*J. Text. Inst. Manchr, Trans.*, 1955, **35** [3], T214–224).—The volumetric method of Kullgren and Tyden (*Ing. Vetenskaps Akad. Handl.*, 1929, **94**, 3) has been modified in order to make it more suitable for chemically treated jute. The distillate is acidified so as to contain 1 per cent. of HCl, treated with bromide - bromate soln. at 21° C for 6·5 min., and the unchanged Br is determined iodimetrically. Variations in the method of distillation or estimation exert no significant effect on the yield of furfuraldehyde. The presence of formaldehyde causes no interference. The apparent yield of furfuraldehyde from jute also includes hydroxymethylfurfuraldehyde from hexose residues (1·2 per cent.).

L. VALENTINE

2489. **Determination of Ardil in Ardil - wool mixtures.** M. V. Glynn (*J. Text. Inst. Manchr, Trans.*, 1955, **46** [3], T228–230).—Wool is less soluble in boiling *N* HCl than Ardil, which dissolves completely in 45 min., and this difference in solubility is sufficient to enable analyses of wool - Ardil blends to be made. Allowance has to be made for the solubility of wool in the reagent. Bleaching and chlorination also increase the solubility of the wool, so complicating the test.

L. VALENTINE

2490. **Qualitative and quantitative analysis of mixtures of surface-active agents, with special reference to synthetic detergents.** C. Kortland and H. F. Dammers (*J. Amer. Oil Chem. Soc.*, 1955, **32** [2], 58–64).—An identification scheme for surface-active agents is presented which enables these agents or their mixtures to be detected in commercial products. The scheme makes use of the main division into anion-active, cation-active and non-ionic substances and the separate analysis of each group. The method can be employed for quant. analysis, and results from a prepared mixture illustrate the accuracy of the method.

D. BAILEY

2491. **Determination of silicic acid in detergents.** E. Heinerth (*Fette u. Seifen*, 1954, **56** [8], 595).—A weighed sample of detergent (2·5 g) is added with stirring to 5 ml of conc. H_2SO_4 (sp. gr. 1·84) in a beaker; 2·5 g of $NaNO_3$ are added and the covered beaker is heated on a hot-plate until the mass is bright yellow and homogeneous; heating for 20 min. is usually sufficient, but it may be necessary to add more $NaNO_3$. The soln. is cooled, carefully diluted with about 100 ml of water,

boiled to remove nitrous gases and filtered through coarse paper. After being washed, the filter and its contents are dried and carefully incinerated at 800° C in a porcelain crucible. The residue is practically pure SiO_2. E. HAYES

2492. **Acceleration of the method for determining double bonds in synthetic resins by means of a catalyst.** T. N. Kasterina, E. N. Fedotova and O. S. Shevchenko (*Zavod. Lab.*, 1955, **21** [4], 408–410).—The use of a 2·5 per cent. solution of mercury acetate in glacial acetic acid as a catalyst greatly shortens the time required for bromination of allyl groups in the pyridine sulphate - bromide method. It is applicable also to the determination of furfuryl alcohol, *e.g.*, in Angell's method (*Analyst*, 1947, **72**, 178); the time necessary for bromination can be cut down from 1 hr. to 1 min. The catalyst (10 ml) is added immediately after the brominating reagent (50 ml of 0·1 *N* bromine equivalent).

G. S. SMITH

2493. **Qualitative reactions for epoxy resins.** M. J. Foucry (*Peint-Pigm.-Vern.*, 1954, **30** [11], 925).—The resin (1 g) is dissolved without heating in 100 ml of H_2SO_4 (66° Bé). The following reactions are given by 1 ml of this solution: (*a*) On adding 1 ml of HNO_3 (40° Bé), shaking, leaving for a few minutes and then pouring into 100 ml of *N* NaOH, an intense orange - red coloration is obtained. (*b*) Addition of 1 to 2 drops of 40 per cent. formaldehyde solution leads to the development of an orange colour, which changes to violet - blue on dilution with water. (*c*) Denigès sulphomercuric reagent (5 ml) gives an immediate yellow ppt. (*d*) $Fe_2(SO_4)_3$ solution (5 ml of 10 per cent.) gives an immediate blackish ppt. These colour reactions are also given by a dry film of an epoxy-resin paint (containing TiO_2 as pigment). The specificity has not yet been fully investigated.

D. R. DUNCAN

2494. **The detection of fillers in phenol - formaldehyde mouldings.** J. Haslam and R. V. Hill (*Analyst*, 1955, **80**, 317).—The method of Esch *et al.* (*Brit. Abstr. B*, 1938, 1450) in which the finely divided material is heated with molten 1- or 2-naphthol for 8 to 24 hr. at 160° to 180° C, followed by solvent extraction to separate the insol. filler, although successful with lightly cured mouldings is often unsatisfactory with highly cured material, mainly owing to imperfect contact with the molten naphthol. The following modification serves for all kinds of material. The portion of ground material passing 30 B.S. sieve and retained on 60 B.S. sieve is suitable. The sample (0·1 g) and 5 g of 2-naphthol are sealed in a Pyrex-glass tube (30 cm × 13 mm), which is then placed in the continuous shaking apparatus (Haslam *et al.*, *Anal. Abstr.*, 1954, **1**, 998). The tube and its contents are then maintained in an oven at 160° to 180° C for 4 hr., with constant rotation of the tube. The cooled tube is opened and the product is treated with 50 ml of ethanol to dissolve the naphthol. The mixture is centrifuged and the insol. residue is washed first by decantation with ethanol until colourless, and finally with ether. The dried filler is weighed. Microscopical examination serves to identify wood flour, coconut-shell flour, and glass, asbestos and cotton fibres. With nylon-filled mouldings, 66 nylon may be present as smooth fibres. Solution of the residue in 90 per cent. formic acid and infra-red examination of the film will confirm this. Neoprene filling yields a rubber-like residue containing Cl, and infra-red examination of a film cast from benzene will often yield conclusive evidence of its presence. A. O. JONES

2495. **A new simple method for determining hydrochloric acid from the thermal decomposition of poly(vinyl chloride).** H. Kiyota and T. Yamamoto (*Japan Analyst*, 1955, **4** [1], 16–21).—The determination of HCl resulting from the thermal decomp. of poly(vinyl chloride) provides a good criterion of the thermal stability of the material. A new rapid method is proposed. The sample powder (0·5 g) is mixed well with pptd. $CaCO_3$ ($\simeq$ 10 g free from Cl), placed in a porcelain crucible, covered with a further 10 g of $CaCO_3$ and heated in an oven (for the thermal stability test, 200° C, 30 min.; for the determination of total Cl, 500° C, 1 hr.). After being cooled, the $CaCO_3$ is dissolved in dil. HNO_3, filtered and treated with a known excess of standard $AgNO_3$ soln. AgCl is filtered off and excess of Ag is determined in the filtrate by KSCN titration. By changing the conditions of heating, the thermal properties of other materials can be studied. The results compared favourably with those obtained by the A.S.T.M. method.

K. SAITO

2496. **Identification of curing agents in rubber products. Ultra-violet absorptiometric analysis of selective solvent extracts.** K. E. Kress and F. G. S. Mees (*Anal. Chem.*, 1955, **27** [4], 528–534).—A method is presented for identification of accelerators used in the vulcanisation of rubber products. Identification is made by u.v. spectrophotometric absorbance curves over the 220 to 380-mμ region on the aq. alkali or acid extracts or on ether extracts of the aqueous soln. Thiazole, thiuram, thiocarbamate, amine and guanidine classes of accelerator are readily identified in as little as 2 g of rubber. Aromatic thiazoles give a max. at 308 mμ in alkali, and aliphatic thiazoles 294 to 298 mμ in soln. alkaline to litmus. Thirty-two accelerators are listed with the appropriate wavelengths. Interference of common softeners and antioxidants is usually neglible. The method may be placed on a quant. basis if calibrations are undertaken. G. P. COOK

2497. **Use of radioactive sulphur for the study and control of the vulcanisation process.** Z. N. Tarasova, M. Ya. Kaplunov and B. A. Dogadkin (*Zavod. Lab.*, 1955, **21** [4], 396–397).—To determine combined sulphur in rubber during manufacture, a proportion of the ^{35}S isotope is added to the vulcanising agent and the β-radiation intensity of discs 20 mm in diameter (0·3 mm thick for soft rubber) is measured with a Geiger - Müller counter after the free sulphur has been removed with hot acetone. The combined sulphur content is read from a calibration graph. The mean error is about 1 per cent. The operational time for a determination is only 8 to 10 min., but the extraction of the free sulphur takes 50 hr. G. S. SMITH

See also Abstract 2570.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

2498. **Chromatographic estimation of different kinds of human haemoglobin.** H. K. Prins and T. H. J. Huisman (*Nature*, 1955, **175**, 903–904).—A full description is given of two procedures for the

separation and quant. determination of the carboxy-haemoglobin-A (adult), B (sickle-shell), C and F (foetal) fractions in human haemoglobin. In the elution method the sample is chromatographed on a column (13 cm × 0·9 cm) of pretreated Amberlite IRC-50 (XE-64) at 10° C and pH 6·5 (citrate buffer of const. citric acid concn. and varying Na^+ concn.), at a relatively low rate of flow. Yields are ≃ 85 per cent. In the second method the sample is chromatographed at 0° C in a flat Lucite cuvette (3 cm × 0·5 cm × 20 cm) filled to 15 cm with the Amberlite resin; the buffer is Na citrate - citric acid (Na^+ concn. 0·15) at pH 6. After elution of 200 ml of eluate (flow rate ≃ 20 ml per hr.) a good separation of the four components is obtained, the respective amounts being determined by measuring a diapositive of the cuvette according to the Grassmann - Hannig method. The deviation from calculated values is ≃ 2 per cent. for the elution method and slightly higher for the cuvette method. The procedures give a clear separation of foetal haemoglobin (even at contents of < 10 per cent.), and enable an abnormal haemoglobin to be eluted free of other pigments. W. J. Baker

2499. **Some observations on impurities present in samples of Evans Blue (T 1824) [azovan blue] and their influence on blood volume determinations effected by the dye method.** G. Cooley (*J. Physiol.*, 1954, **123**, 16).—A red impurity is present in the commercial dye which absorbs light in the region of the maximum of the main blue component. Erroneous results are thus obtained especially as, in addition, the red dye disappears from the blood faster than the blue dye. The dyes can be separated from each other on alumina columns by the method of Leeson and Reeve (*J. Physiol.*, 1951, **115**, 129). E. Kawerau

2500. **The stabilisation of ammonium purpurate for colorimetric use.** F. W. Diggins (*Analyst*, 1955, **80**, 401–402).—The colorimetric determination of Ca by the method of Williams *et al.* (*Anal. Abstr.*, 1954, **1**, 249) is based on the colour change exhibited by ammonium purpurate (murexide) in the presence of Ca in alkaline soln. and the reagent contains ethanol to stabilise it. In an application of the method to biological fluids a serious progressive fading of the colour of standard solutions of $CaCl_2$ occurred in the spectrophotometer. The stability of the reagent has been improved by using 2-methoxyethanol in place of ethanol. Ammonium purpurate is not sufficiently soluble in this to give the required absorption, and it is necessary to dissolve it first in a little water and dilute the filtered soln. with 2-methoxyethanol. The method has also been modified to allow the use of this solvent as a diluent for the solutions for colorimetry. The absorption readings are constant for at least 30 min. and it is not necessary to add the ammonium purpurate reagent to the Ca soln. within 5 min. of adding it to the blank. Details of the method will be published later. A. O. Jones

2501. **Clinical significance of the magnesium : calcium ratio. Technique for the determination of magnesium and calcium in biological fluids.** H. S. Friedman and M. A. Robin (*Clinical Chemistry*, 1955, **1** [2], 125–133).—Calcium and magnesium are determined by titration with EDTA (**I**), with Eriochrome black T (0·5 g in 100 ml of water) as indicator. *Total bivalent ions*—To 0·5 ml of standard or unknown soln. (serum or spinal fluid) add 4 ml of water, 0·5 ml of buffer (pH 10) (67·5 g of NH_4Cl and 570 ml of aq. NH_3, sp. gr. 0·88, in water to 1 litre) and 2 to 4 drops of indicator. Titrate with standard **I** until the colour changes from pink to pure blue. *Magnesium*—To 1 ml of serum or spinal fluid in a 15-ml centrifuge tube add 2·5 ml of water and 0·5 ml of buffered oxalate soln. (35 g of NH_4Cl, 1·5 g of NH_4 oxalate and 3·5 ml of aq. NH_3, sp. gr. 0·88, in water to 250 ml). Mix, set aside for 30 min. and centrifuge at 2500 r.p.m. for 10 min. Titrate 2 ml of the supernatant liquid as before. *Standards*—Dissolve 50 mg of magnesium powder in 600 ml of water and 50 ml of 0·1 *N* HCl and dilute to 1 litre with water. This soln. contains 4·12 milli-equiv. of Mg per litre. For stock **I** soln., dissolve 750 mg in the min. amount of 0·1 *N* NaOH and dilute to 1 litre with water. For use, dilute this soln. 1 to 10 with water and standardise against the magnesium standard so that 1 ml is equiv. to ≃ 0·5 milli-equiv. per litre. H. F. W. Kirkpatrick

2502. **Method for the spectrographic determination of silicon in blood.** P. E. Sȳrkina (*Gigiena i Sanitariya*, 1954, [6], 45–47; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 49,802).—A method is described for the direct spectrographic determination of silicon in blood by combustion in the condensed spark. Copper electrodes are used and the lower hollow electrode is connected to a vessel containing blood haemolysed by saponin and mixed with an equal vol. of 26 per cent. $K_3Fe(CN)_6$ soln. The Si spectrum is obtained on a background of Fe lines, and the Si content is determined from a calibration curve constructed for the Si line 2516·1 A. The error is ± 10 per cent. E. Hayes

2503. **Micro-estimation of cyanide with a modified Epstein procedure.** K. Jørgensen (*Acta Chem. Scand.*, 1955, **9** [3], 548).—By modifying the prep. of reagents used in the Epstein method (*Brit. Abstr. C*, 1947, 117), the sensitivity is increased five- to six-fold so that CN′ concn. of 10^{-5} to 10^{-6} *M* can be determined to within 3 per cent. The pyridine - pyrazolone reagent (**I**) is prepared by dissolving 150 mg of a powdered mixture (5 + 1, by wt.) of 3-methyl-1-phenyl-5-pyrazolone and the corresponding bis-compound in 25 ml of pyridine; the solution is stable for one week at 0° C. The bis-pyrazolone is prepared by gently refluxing a (1 + 3) mol. mixture of ethyl acetoacetate and phenylhydrazine for ≃ 25 min. and extracting the solid product with boiling ethanol. *Procedure*—Mix 4 ml of the sample (pH 4 to 8) with 0·2 ml of 0·5 per cent. aq. chloramine T and, after 5 min. (keeping all solutions at ≃ 0° C), add 0·8 ml of **I**. Keep the mixture at room temp. for 80 to 90 min. before measuring the intensity of the blue coloration at 632 mμ; the final extinction varies from 1·0 to 0·1, Beer's law being valid. A known standard is always run simultaneously. W. J. Baker

2504. **Blood-sugar determination with thymol - sulphuric acid.** J. Schmör (*Klin. Wochschr.*, 1955, **33** [17–18], 449–450).—To 1·9 ml of 6 per cent. trichloroacetic acid in a centrifuge tube add 0·1 ml of blood, plasma or serum, mix and centrifuge. Prepare a blank with 0·1 ml of water in place of blood. Dilute 1 ml of clear supernatant liquid in a test-tube with 1·5 ml of water and add slowly, with mixing and cooling in running water, 5 ml of thymol - H_2SO_4 reagent [250 mg of thymol dissolved in 100 ml of conc. H_2SO_4 (sp. gr. 1·84)]. Heat in boiling water for 10 min., cool and measure the rose colour at 500 or 530 mμ. Standards for up to

500 mg per cent. of glucose showed a linear relation between E and concn. The average error of a single determination was 2·5 per cent. and the method appears to be highly specific for glucose.
H. F. W. KIRKPATRICK

2505. **Blood-sugar determinations of the honey bee by paper chromatography.** C. von Czarnowski (*Naturwissenschaften*, 1954, **41** [24], 577).—By the older methods glucose alone could be demonstrated in the blood of the bee. Chromatography revealed that the remaining reducing fraction was fructose. The total blood-sugar is 1700 to 3700 mg per 100 ml. The blood of young worker bees had an average total blood sugar of 2000 to 2300 mg per 100 ml, of which fructose was ≃ 800 to 1000 mg per 100 ml. The blood of young queen bees contained up to 35 per cent. of fructose. E. KAWERAU

2506. **Determination of glucose in the presence of amino acids and other nitrogenous compounds.** K. Müller and K. Täufel (*Z. anal. Chem.*, 1955, **145** [2], 98–102).—The glucose in mixtures of this substance with amino acids (glycine, DL-alanine, DL-*iso*leucine, DL-tyrosine, L-cystine), *p*-aminobenzoic acid, nicotinamide and glucosamine was determined by the ceric sulphate method and by the hypoiodite method in order to discover the effect on the reduction value of different quantities of the nitrogenous compounds. In the ceric sulphate titration, *p*-aminobenzoic acid colours the solution and makes it difficult to judge the end-point. Tyrosine and cystine affect the reduction, but the other compounds have no effect. With the hypoiodite method, nicotinamide has no effect. With glycine, alanine and *iso*leucine, somewhat high results are obtained, but these are due to the reaction between the hypoiodite and the amino acids and not to any reaction between the amino acids and glucose. A. J. MEE

2507. **Determination of salicylic acid and two metabolites in plasma and urine using fluorimetry for directly measuring salicyluric acid.** E. B. Truitt, jun., A. M. Morgan and J. M. Little (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [3], 142–148).—A quant. method is described for the determination of salicylic acid (**I**) and salicyluric acid (**II**) in plasma, and of **I**, **II** and salicyl glycuronates (**III**) in urine. *Procedure*—Determine **I** colorimetrically with $Fe(NO_3)_3$ at 540 mμ by using a CCl_4 extract of the acidified sample; no correction for interference by **II** is normally necessary. Determine **II** by extracting the acidified sample with a 1·5 per cent. soln. of *iso*pentanol in 1:2-dichloroethane, extracting the organic phase with buffer (pH 10), and measuring the fluorescence of the buffer phase by using 370-mμ primary and 460-mμ secondary filters; a correction must be applied for the slight fluorescence of **I**. Determine **III** by controlled hydrolysis with HCl, correcting for the **I** present and for the **II** (62 per cent. hydrolysed under these conditions). A. R. ROGERS

2508. **The blood-level determinations of *p*-amino-salicylic acid and isoniazid with vanillin.** E. N. Deeb and G. R. Vitagliano (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [3], 182–185).—A method is described for the determination of either 4-amino-salicylic acid (**I**) or isoniazid (**II**) in oxalated blood plasma or serum. Recovery experiments indicate an accuracy of ± 0·9 per cent. for **I** and ± 0·4 per cent. for **II**. Streptomycin, dihydrostreptomycin and viomycin do not interfere, but **I** and **II** interfere in the determination of each other. *Procedure*—For **I**, dilute the sample (2 ml) with H_2O (10 ml), add 20 per cent. trichloroacetic acid (4 ml), shake vigorously, centrifuge and filter through a fine paper; to 8 ml of protein-free filtrate in a cell (19 mm × 150 mm) add a 10 per cent. soln. of vanillin in 50 per cent. ethanol (1 ml), 5 *N* H_2SO_4 (1 ml), mix, and measure the extinction at 410 mμ after 10 min. For **II**, dilute the sample (4 ml) with H_2O (4 ml), add 20 per cent. trichloroacetic acid (8 ml), shake, centrifuge and filter; to 8 ml of filtrate add 2 per cent. vanillin in 25 per cent. ethanol (1 ml) and *N* H_2SO_4 (1 ml), and read at 400 mμ after 10 min. A. R. ROGERS

2509. **Simple paper-chromatographic technique for the study of free metabolites of tissues and body-fluids.** G. Ceriotti (*Nature*, 1955, **175**, 897–898).—The modified paper-disc chromatographic procedure described involves the use of serum or tissues dried at 100° C and powdered; it enables the free metabolites to be extracted completely from the broken cells and to be identified even when present in very small amounts. A sheet of Schleicher and Schüll 2043b filter-paper is placed between two glass plates (25 cm × 25 cm), one of which has a central hole (6 mm in diam.) in which the sample (5 to 10 mg of tissue or 15 to 20 mg of serum) is distributed evenly and covered with a filter-paper disc lightly wetted with the solvent. The plate is then inverted carefully over a small dish containing the wick, a filter-paper cone, the base of which is immersed in 10 ml of solvent. The space between dish and plate becomes saturated with solvent vapour, the solvent flowing regularly through the sample during extraction and chromatography. The solvent is allowed to flow 10 cm from the centre of the cone; this takes ≃ 7 hr. with a solvent mixture of *n*-butanol, water and acetic acid (4:4:1), or ≃ 12 hr. with a mixture of *tert.*-butanol, formic acid and water (70:15:15), very good separation being attained. The dried chromatograms can be examined by the usual methods. W. J. BAKER

2510. **Influence of formic acid on the hydrolysis of tissue proteins. A new and rapid method of hydrolysis of proteins.** S. W. Gurnani, U. S. Kumta and M. B. Sahasrabudhe (*Biochim. Biophys. Acta*, 1955, **16** [4], 553–557).—This method shortens the time required for hydrolysis of proteins without impairing the release of amino acids. Tissue is homogenised and boiled with 85 per cent. formic acid (2 ml per g of tissue). When solution is complete (2 to 3 min.), 2 *N* HCl is added to a final volume of 20 ml per g of tissue, and the mixture is refluxed for 2 hr. Increasing the time up to 6 hr. does not increase the amino-acid yield, which is equiv. to that from 20 hr. hydrolysis with 2·5 *N* HCl. Some loss of added tryptophan was observed and an alkaline hydrolysis is recommended for estimation of this compound. Serum proteins can be treated by this technique. The microbiological assay of the derived amino acids is not affected by this process. G. W. CAMBRIDGE

2511. **Chromatography of serum and other proteins on an anion-exchange resin.** H. G. Boman (*Nature*, 1955, **175**, 898–899).—In the procedure described, Dowex 2 (200 to 400 mesh) in chloride form is used as adsorbent and tri(hydroxymethyl)methylamine hydrochloride as buffer. The proteins are adsorbed at low ionic strength on a column (18 cm × 1·5 cm) at 4° C and eluted by a stepwise increase (from 0·02 to 1 *M*) in buffer

concn. at a const. buffer pH of 7·2. Fractions (vol. ≃ 3·3 ml) are removed every 30 min. Results for (*i*) human-serum albumin and (*ii*) serum from a patient with prostatic cancer are reported and discussed. The method can be used also for purifying crude vegetable acid-phosphatase and for separating prostatic phosphatase, haemoglobin, phycoerythrin and phycocyanin. W. J. BAKER

2512. **The isolation and estimation of urinary mucoproteins.** A. J. Anderson and N. F. Maclagan (*Biochem. J.*, 1955, **59** [4], 638–644).—A colorimetric method for the determination of urinary mucoproteins in normal and pathological urines is described. The mucoprotein is adsorbed on benzoic acid and, after removal of benzoic acid with acetone, the residual mucoprotein is dissolved in water adjusted to pH 9 to 9·5. When this solution is mixed with a diphenylamine soln. (1 g of diphenylamine in a mixture of 19 ml of glacial acetic acid and 10 ml of conc. H_2SO_4), and heated at 100° C for 30 min., a purple colour is formed. This is measured photo-electrically with a spectrum green filter (520 mμ) and the amount of mucoprotein is ascertained from a calibration graph.
J. N. ASHLEY

2513. **Protein-bound iodine by alkaline incineration and a method for producing a stable "cerate" colour.** A. Grossmann and G. F. Grossmann (*J. Clin. Endocrinol. and Metabolism*, 1955, **15** [3], 354–361).—An alkaline incineration method for the determination of protein-bound iodine in serum is described in detail. The method is essentially that of Barker *et al.* (*J. Clin. Invest.*, 1951, **30**, 55) except for the final colorimetric step, in which the "cerate" colour (formed with a ceric salt) is stabilised for photometer reading by the addition of brucine sulphate soln. to the cooled reaction mixture. H. F. W. KIRKPATRICK

2514. **Purification of chromium (VI) for use in the PBI [protein-bound iodine] determination.** W. B. Mason and S. Coco (*Clinical Chemistry*, 1955, **1** [2], 117).—For use in the determination of serum protein-bound iodine, CrO_3 may be practically freed from iodine by conversion into chromyl chloride by the method of Fernelius (*Inorg. Synth.*, 1946, **II**, 205); the crude CrO_2Cl_2 is diluted with water and used with conc. H_2SO_4 for the combustion. H. F. W. KIRKPATRICK

2515. **Paper electrophoresis of steroid derivatives.** W. P. McKinley (*Science*, 1955, **121** [3135], 139–140).—Hydrazones were prepared by refluxing 2·5 mg of steroid with 7·0 mg of Girard's T reagent in 2 ml of 10 per cent. acetic acid in methanol for 2 hr. The apparatus and technique for paper electrophoresis were as previously described for lipoproteins (*Anal. Abstr.*, 1954, **1**, 2767). The solvent system was 0·05 *M* sodium borate and the current 1·5 mA per in. width of strip at 200 V. The hydrazones were detected by viewing the dried strip under the u.v. lamp, followed by dipping in Kraut - Dragendorff reagent (Block *et al.*, "A Laboratory Manual on Paper Chromatography," Academic Press, N.Y., 1952). The relative mobilities of the hydrazones observed were: progesterone 1·00, androsterone 0·85, deoxycorticosterone 0·83, methyltestosterone 0·77, ethisterone 0·76, testosterone 0·75, oestrone 0·53.
H. F. W. KIRKPATRICK

2516. **X-ray diffraction powder data for steroids.** J. Parsons and W. T. Beher (*Anal. Chem.*, 1955, **27** [4], 514–517).—X-ray diffraction powder data and powder diffraction photographs for 27 steroids are presented. Visual comparison of the powder patterns for known and unknown steroids was found to be sufficient for identification.
G. P. COOK

2517. **A contribution to the chromatography of oestrogens.** H. Breuer (*Naturwissenschaften*, 1955, **42** [1], 16).—Good separation of oestrogens is obtained on 60-mm columns of standardised Brockmann alumina by using a form of gradient-elution technique. The eluting agent is a benzene - ethanol mixture which, beginning with an ethanol concentration of 0·1 vol. per cent., is enriched by ethanol by 0·1 vol. per cent. for every successive 100 ml of the mixture used. Oestrone is thus eluted at an ethanol concn. of 0·2 to 0·5 vol. per cent., β-oestradiol at 0·6 to 0·7 and oestriol at 15 to 20 vol. per cent. With 5 to 40 μg of synthetic hormone mixture on the column the average recovery for oestrone was 98, β-oestradiol 96 and oestriol 85 per cent. No trailing of the fronts took place. E. KAWERAU

2518. **Counter-current distribution procedure for the quantitative - qualitative analysis of small amounts of urinary corticosteroids.** N. B. Talbot, S. Ulick, A. Koupreianow and Z. Zygmuntowicz (*J. Clin. Endocrinol. and Metabolism*, 1955, **15** [3], 301–316).—The method described comprises extraction of the corticosteroids with $CHCl_3$, fractionation of the residue from the washed $CHCl_3$ extract by counter-current distribution, and spectrophotometric determination of the steroids by means of the thiosemicarbazide reaction.
H. F. W. KIRKPATRICK

2519. **The influence of chloride on the oxidation of adrenocortical steroids by sodium bismuthate.** D. C. Smith and S. L. Tompsett (*Analyst*, 1955, **80**, 397–399).—In a study of the products of oxidation of corticosteroids by sodium bismuthate, Brooks *et al.* (*Anal. Abstr.*, 1954, **1**, 131) found that only those steroids with side-chains characteristic of cortisone (also its reduced form) and pregnanetriol are oxidised by the bismuthate in 50 per cent. aq. acetic acid to produce substances that give the characteristic colour effect of the 17-ketosteroids in the Zimmermann reaction. Subsequently Norymberski *et al.* (*Lancet*, 1953, **i**, 1276) measured the increase in the 17-ketosteroid content of urine after treatment with sodium bismuthate. This fraction, designated the 17-ketogenic steroids, is believed to include only those steroids chemically related to cortisone and pregnanetriol. The effect of possible interfering substances normally present in urine has apparently not been investigated. It is now found that the presence of Cl′ (ranging in urine from traces to 1 per cent.) may cause serious errors, owing to the formation of free Cl. Experimental work on the determination of steroids in the presence or absence of Cl′ showed that although it has no effect on the oxidation of cortisone it does appear to be responsible for the production of 17-ketosteroid-like chromogenic material from substances other than cortisone (*e.g.*, *allo*pregnanediol and androstanediol). Conjugates of the 17-ketosteroids are completely separated from urine by extraction with ethanol - ether in the presence of $(NH_4)_2SO_4$ (Edwards *et al.*, "Memoirs of the Society for Endocrinology, No. 2," Dennis Dobson Ltd., London, 1953, p. 53). Such

extracts, which are chloride-free, also contain conjugates from which the fraction referred to as the 17-ketogenic steroids is derived. Application of the bismuthate reaction to these extracts rather than to untreated urine appears to be necessary. The clinical use of this procedure is under investigation. A. O. JONES

2520. **Steroids. XIII. Paper chromatography of steroid amines.** Ž. Procházka, L. Lábler and Z. Kotásek (*Chem. Listy*, 1954, **48** [7], 1066–1070).—The paper chromatography of a number of lipophilic steroid amines is described. Amines containing one nitrogen atom were separated by means of moist butyl acetate or the solvent system light petroleum (as stationary phase) - aq. ethanol. The separation of the steroid alkaloids from the bark of *Holarrhena antidysenterica* was effected by the systems pentanol - acetic acid - water (top layer) or water-saturated, weakly acid *sec.*-butanol on paper impregnated with KCl, or, best, light petroleum - aq. alkaline ethanol. The spots were detected by iodine vapour or the Kraut - Dragendorff reagent. G. GLASER

2521. **Colorimetric determination of blood arginase.** M. M. Friedman and E. Becker (*Clinical Chemistry*, 1955, **1** [2], 110–116).—*Haemolysis*—To 1·0 ml of oxalated blood add 9·0 ml of saponin soln. (0·05 per cent.), mix and set aside at room temp. for 30 min. *Activation*—Add 0·5 ml of 20 per cent. $MnCl_2.4H_2O$ soln. and set aside for 2 hr. Place 2·0-ml aliquots in test-tubes T_1 (for total urea) and T_2 (for preformed urea); to T_1 add 1 ml of arginine substrate (9 g of L-arginine monohydrochloride, Merck, and 3·2 ml of CO_2-free 9 *N* NaOH in water to 50 ml) and incubate at 25° C for exactly 10 min. Add 2 ml of 15 per cent. trichloroacetic acid (**I**). To T_2 add 2 ml of **I**, then 1 ml of arginine substrate. Shake both tubes, set aside for 15 min. and filter. A reagent blank is made by mixing 0·1 ml of $MnCl_2$ soln., 1·9 ml of saponin soln., 2 ml of **I** and 1 ml of arginine substrate, shaking and filtering. *Urea determination*—To 2 ml of each filtrate add 15 ml of H_2SO_4 - H_3PO_4 (90 ml of conc. H_2SO_4 and 270 ml of 85 per cent. H_3PO_4 in water to 1 litre) and mix. To 10-ml aliquots in Pyrex-glass test-tubes add 0·5 ml of *iso*nitrosopropiophenone (3 per cent. in 95 per cent. ethanol), close with rubber stoppers carrying short capillaries (0·5 to 1·0 mm bore), and place in boiling water for 1 hr. in the dark. Remove and place in a bath at 50° to 55° C, read in warm cuvettes at 540 mμ against the blank. *Standards*—Dilute 1 to 6 ml of working standard (1 ml of urea soln., 67·3 mg in 100 ml of water, added to 24 ml of H_2SO_4 - H_3PO_4 mixture) to 9 ml with H_2SO_4 - H_3PO_4 mixture; to each add 1 ml of arginine - **I** (5 ml of arginine substrate mixed with 10 ml of **I** and 5 ml of water) and determine the urea as before with 9 ml of H_2SO_4 - H_3PO_4 and 1 ml of arginine - **I** as blank. 1 ml of working standard ≡ 10 blood arginase units. The result is given by $T_1 - T_2$. With 100 normal adults a range of 30·1 to 83·1 units was obtained. H. F. W. KIRKPATRICK

2522. **Polarographic determination of trypsin activity.** Š. Štokrová (*Chem. Listy*, 1954, **48** [7], 1082–1084).—From the data obtained by following polarographically the degradative action of standard trypsin solutions on a protein, by means of the protein double wave formed in ammoniacal solutions of cobalt, a calibration graph was constructed, from which the relative value of the trypsin activity could be determined. *Procedure*—To six 0·5-ml samples of a 3 per cent. aq. soln. of albumin add consecutively, and in known time intervals, 0, 0·1, 0·2, 0·3, 0·4 and 0·5 ml of a standard soln. of trypsin, dilute each to 1·5 ml with a buffer soln. (0·1 *M* NH_4Cl and 0·1 *M* aq. NH_3) and maintain at 35° C for 20 min. Take a 0·5-ml aliquot from each sample, add it to 1 ml of a 20 per cent. soln. of sulphosalicylic acid, filter off the ppt. of unchanged protein, add 0·2 ml of the filtrate to 4 ml of a mixture of 0·001 *M* $[Co(NH_3)_6]Cl_3$, 0·1 *M* NH_4Cl and *M* aq. NH_3, and polarograph at 25° C from − 0·8 V. G. GLASER

See also Abstracts 2578, 2586, 2599, 2605.

Drugs

2523. **Experiments relating to the quantitative determination of alkaloids on electropherograms.** P. H. List (*Naturwissenschaften*, 1954, **41** [19], 454).—The method is applicable to alkaloids that migrate in an electrical field without suffering decomposition, and that produce a poorly soluble complex with molybdophosphoric acid. Atropine is used as test substance. Electrophoresis is carried out in 10 per cent. formic acid for 3 hr. Air-dried strips are dipped for a short period into a molybdophosphoric acid reagent (1 g of molybdophosphoric acid and 2 ml of conc. HNO_3 added to 98 ml of water). The strips are washed for 10 min. in slowly running water, air-dried and immersed in a bath of $SnCl_2$ soln. (1 g in 100 ml of 3·8 per cent. HCl) and again dried at room temp. The strips are rendered translucent by immersion in a mixture of equal parts of 1-bromonaphthalene and paraffin and scanned on a photo-electric instrument. The area of the extinction curves is linear to the concentration of the alkaloid over a wide range of concentrations. E. KAWERAU

2524. **Spectrophotometric determination of the principal alkaloids of opium.** M. S. Dyer and A. J. McBay (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [3], 156–160).—The u.v. spectra of narceine (**I**), narcotine (**II**), papaverine (**III**), and thebaine (**IV**) and its acid decomposition products were determined at various pH values. A method of assay for samples of opium concentrates is proposed that needs less time and a smaller sample than the existing methods, and gives satisfactory results. It is based on the following separations: aqueous NaOH extracts codeine (**V**), morphine (**VI**) and **I**, but not **II** and **III** from $CHCl_3$ soln.; **IV** appears in both phases. Benzene extracts **IV** and **V**, but not **I** and **VI** from NaOH soln. Hydrolysis with ethanolic KOH permits extraction of **II** but not **III** and **IV** from benzene with aq. NaOH. The alkaloids are determined by u.v. spectrophotometry by using the wavelengths 278 mμ and 300 mμ for **I** and **VI** in *N* NaOH, 265 mμ and 285 mμ for **IV** and **V** in dil. H_2SO_4, 285 mμ and 312 mμ for **III** and **IV** in dil. H_2SO_4, and 312 mμ for **II** in dil. HCl. A. R. ROGERS

2525. **Detection of opium alkaloids on paper chromatograms.** G. Csobán and I. Hegedüs (*Magyar Kém. Foly.*, 1954, **60** [4], 121–122; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 50,273).—The paper chromatogram of opium alkaloids is treated with Mayer's reagent, excess of the reagent is washed off with tap-water, and the pptd. Hg is detected as HgS by means of ammonium sulphide soln. E. HAYES

2526. **Methods for the determination of protoveratrine.** E. W. Grant and E. E. Kennedy (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [3], 129–132).—Titrimetric (in aq. or non-aq. solvents) and i.r. methods (with the 5·8-μ band) of determining protoveratrine are not specific, and do not distinguish protoveratrine A (**I**) from protoveratrine B (**II**). Counter-current distribution, adsorption chromatography (on Al_2O_3) and i.r. methods (by use of slight differences in spectra between 8 and 10 μ) of determining **I** and **II** separately in mixtures of veratrum alkaloids are unsuitable for routine control use. A paper partition chromatographic method is described which gives satisfactory recoveries of each of **I** and **II** in the presence of minor alkaloidal impurities. Strips ($\frac{1}{2}$ in. × 22 in.) are used for < 600 μg of sample, which is developed with a saturated soln. of formamide in benzene for 20 hr. The positions of the bands (**II** is non-mobile) are found on a control strip by the orange coloration with Dragendorff's reagent. The relevant portions are cut from sample and blank strips, eluted with ethanol (15 ml each), the eluates are evaporated to dryness, dissolved in H_2SO_4 (5 ml each), and determined separately by measuring the extinction at 540 mμ after 18 hr.

A. R. ROGERS

2527. **Paper-chromatographic detection of hellebrin (Roche).** G. Schenck and H. Sadée (*Arch. Pharm., Berlin*, 1955, **288** [3], 101–102).—In a paper-chromatographic detection of hellebrin, a pentanol - water (1 + 1) mixture, as recommended by Tschesche, Grimmer and Seehofer (*Chem. Ber.*, 1953, **86**, 1235), is used, with $SbCl_3$ (20 per cent.) in chloroform to give a greenish-yellow complex with hellebrin. This colour is as good in daylight as in u.v. The R_F value of 0·79 (0·78 to 0·80) for hellebrin is reproducible using 10 to 50 μg on S & S 2043a paper with a pentanol - water (1 + 1) mixture, developed downwards after 6 hr. (≃ 30 cm). It is a single substance which, under these conditions, gives well-defined spots.

R. STERN

2528. **Quantitative determination of allicin in fresh garlic.** H. Jager (*Arch. Pharm., Berlin*, 1955, **288** [3], 145–148).—The work by Cavallito (*J. Amer. Chem. Soc.*, 1944, **66**, 1950) and Stoll (*Helv. Chim. Acta*, 1948, **31**, 189) on the identification of allicin and alliin is described. Methods for the determination of total sulphur and allicin in fresh garlic are given. *Total sulphur*—On drying there is a loss of sulphur as organic sulphides; the garlic is therefore pre-oxidised with conc. HNO_3, dried and ashed. The sulphate in the ash is then determined. *Allicin*—After enzymatic splitting of allicin, the pyruvic acid formed is determined colorimetrically as the 2:4-dinitrophenylhydrazone. It can be separated from other 2:4-dinitrophenylhydrazones because of its solubility in alkali. Full experimental details of both determinations are given.

R. STERN

2529. **Colorimetric evaluation of thyme and its galenical products.** U. Bogs and J. Meinhard (*Arch. Pharm., Berlin.*, 1955, **288** [3], 134–139).—The official methods (German and Swiss) for the determination of thymol and carvacrol in thyme oil cannot be used for their determination in galenical preparations. A colorimetric method involving diazotisation has therefore been developed. A solution of NaOH (2 per cent.) containing 2 to 4 mg of thymol (3 ml) is coupled with a solution containing sulphanilic acid (0·5 per cent.), H_2SO_4 (2 per cent.), $NaNO_2$ (2 per cent.) (7 ml) (4:1:2). The extinction coefficient (1 cm) is read after 1 min. with a Pulfrich photometer. The maximum was obtained at 470 mμ. In the absence of ethanol the extinction coefficient remained constant for 45 min. Similar results were obtained with thyme oil. With thyme and its preparations a steam distillation from a tartaric acid solution was carried out; distillation from alkaline solutions gave low results. A suitable quantity of the distillate was then treated as above. With suitable modifications this method can be used for other thyme preparations.

R. STERN

2530. **A new colorimetric procedure for the quantitative determination of adrenaline and noradrenaline in the presence of one another.** R. Reiss (*Z. anal. Chem.*, 1955, **145** [4], 265–268).—The method is based on the formation of a stable intense red coloration when adrenaline and noradrenaline are treated with $NaNO_2$ in acid medium and made alkaline. The material (20 to 200 μg) is dissolved in a 25-ml calibrated flask in 5 ml of an HCl - sodium citrate buffer solution at pH 1·9. Exactly 6 min. after the addition of 1 ml of an 0·5 per cent. $NaNO_2$ solution the yellowish-green solution is treated with 3 ml of 30 per cent. aq. NaOH soln. and diluted to the mark with water. After 5 min. the intensity of the colour is measured at 500 mμ against a blank (prepared in the same way without the addition of $NaNO_2$). A second portion of the original material is treated in the same way, except that a pH of 1·1 is used and the period between the addition of $NaNO_2$ and alkali is 8 min. The amount of adrenaline and noradrenaline in the material may be determined from standard curves: the value of the first measurement gives adrenaline and of the second, noradrenaline. For accurate results the conditions described above must be strictly maintained. The limit of detection is 0·5 μg per ml and the method is said to be more specific than others. Results fluctuate within a limit of ± 5 per cent., if the total amount of 200 μg per 25 ml of noradrenaline and adrenaline is not exceeded. Adrenalone gives the same reaction, but not ephedrine nor phenylephrine.

R. J. MAGEE

2531. **Quantitative analysis of oxytetracycline by a polarographic method.** T. Noto and G. Matsuoka (*Japan Analyst*, 1955, **4** [1], 30–34).—A new method for the quant. determination of oxytetracyline is proposed. The sample soln. (≃ 0·02 *M*, pH 2, 1 ml) is treated with HCl (1 + 1, 1 ml) and $NaNO_2$ (3 *M*, 1 ml) at room temp. for 20 min., to obtain an equiv. amount of nitroso-oxytetracycline. This is stable in a basic soln. and shows a distinctive polarographic wave ($E_{\frac{1}{2}}$ = −0·86 V *vs.* the S.C.E.) in NH_4Cl - aq. NH_3 soln. The soln. containing the nitroso compound is neutralised with aq. NH_3 soln. (1 + 1, ≃ 1 ml), treated with 4 *N* NH_4Cl - aq. NH_3 (5 ml), 0·4 per cent. gelatin soln. (0·5 ml) and saturated Na_2SO_3 soln. (2 ml), made up to 20 ml, and submitted to polarography. The wave height is proportional to the concn. within the range 1×10^{-5} to 2×10^{-3} mole per litre. Decomposition products of oxytetracycline (CO_2, NH_3, dimethylamine, benzoic acid, etc.) do not affect the conversion into the nitroso compound, but increase the error by 1 to 3 per cent., owing to the change of the residual current. This method can be applied to various medicinal preparations of oxytetracycline and compares favourably with the

conventional colorimetric method. It also decreases the time necessary for an estimation. K. SAITO

2532. **Discovery, development and antimicrobial properties of D-4-amino-3-*iso*oxazolidone (oxamycin), a new antibiotic produced by *Streptomyces garyphalus* n. sp.** D. A. Harris, M. Ruger, M. A. Reagan, F. J. Wolf, R. L. Peck, H. Wallick and H. B. Woodruff (*Antibiot. & Chemother.*, 1955, **5** [4], 183–190).—A description is included of a cylinder-plate procedure for the assay of D-4-amino-3-*iso*oxazolidone (**I**) in preparations and in *Strep. garyphalus* broth cultures. An agar medium seeded with *Micrococcus pyogenes* var. *aureus* is found suitable for the assay of test solutions containing about 67 μg per ml of **I** in 0·05 *M* phosphate buffer at pH 8·0. A standard curve is prepared daily with pure **I** at concentrations from 16 to 100 μg per ml. After incubation for 17 hr. at 28°C, the zones of inhibition produced are measured, and the potency of the test solution is obtained by reference to a nomogram established from the daily standard curve.

W. H. C. SHAW

2533. **The assay of antibiotics in combination using resistant strains of *Micrococcus pyogenes* var. *aureus*.** A. E. Tanguay, A. B. Bogert and D. C. Wehner (*Antibiot. & Chemother.*, 1955, **5** [4], 232–237).—Details are given for determining each of the four antibiotics in an ointment containing chlortetracycline (**I**) or tetracycline (**II**), procaine penicillin G (**III**), neomycin sulphate (**IV**) and dihydrostreptomycin sulphate (**V**) in a soft paraffin base. A weighed portion of the preparation is treated with light petroleum to remove the soft paraffin, then the residual antibiotics are extracted with dry methanol to which a few crystals of KH_2PO_4 have been added; this solvent dissolves only **I** (or **II**) and **III**. The methanol extract is diluted to a known volume with phosphate buffer, pH 6·0, treated with penicillinase and assayed for **I** with a regular strain of *M. pyogenes* var. *aureus*. The same extract without the penicillinase treatment is assayed for **III** by using a **I**-resistant strain. **IV** and **V**, insoluble in methanol, are dissolved in 0·1 *M* phosphate buffer, pH 8·0, and **IV** is assayed with a **V**-resistant strain of *M. pyogenes* var. *aureus* with a modified pad-plate procedure. **V** can be determined by the *Bacillus subtilis* plate assay method without interference by **IV**.

W. H. C. SHAW

2534. **The separation of organic compounds [drugs] on ion exchangers by selective elution in a closed cycle.** G. Thomas, P. Roland and F. Crucke (*Pharm. Weekbl.*, 1955, **90** [8], 241–251).—The use of ion-exchange resins for the separation of the components or group of components of pharmaceutical mixtures is described. A closed system is used in which percolation of the resin by distillation of appropriate solvents takes place, thus allowing the components to be collected in comparatively small volumes. Types of resins and solvents are discussed and comments are made on the difficulties that may be met in any subsequent spectrophotometric determination. Specific methods, including spectrophotometric determination, are given for (*a*) chloramphenicol in admixture with sulphanilamide, sulphathiazole and propylene glycol, (*b*) codeine in various preparations and (*c*) papaverine, codeine and sodium benzoate in syrups, etc. Recoveries of from 96 to 102 per cent. are quoted for (*b*). K. A. PROCTOR

2535. **Isolation and identification of ethylpiperidinobarbituric acid in forensic chemistry.** F. Dybing (*Acta Pharmacol. Tox., Kbh.*, 1955, **11** [1], 72–78).—Unlike other barbituric acids, ethylpiperidinobarbituric acid (**I**) is not precipitated by $HgSO_4$ in the presence of H_2SO_4, and this method cannot be used for its isolation and purification. Details are given for extraction with ether of barbituric acids not containing a basic group from a dil. H_2SO_4 soln. (pH 1) of the partially purified extract obtained in the conventional Stas - Otto process. The aq. soln. is then adjusted to pH 5 to 6 with Na_3PO_4 and **I** is extracted with ether. The ether extract is dried with anhyd. Na_2SO_4, treated with activated charcoal, and the residue from the filtered soln. is purified by vacuum sublimation. Identification is by u.v. absorption in *N* NaOH, 0·1 *N* H_2SO_4 and in borate buffer at pH 10, by m.p. (222° C) and by the *p*-nitrobenzyl derivative, m.p. 170° C. Details are also given of precipitation and colour reactions for **I** and for descending one-dimensional paper-chromatography. W. H. C. SHAW

2536. **Contribution to the analysis of *iso*nicotinic acid hydrazide [isoniazid] and *p*-aminosalicylic acid.** G. Zinner (*Arch. Pharm., Berlin*, 1955, **288** [3], 129–133).—The separation of *iso*nicotinic acid hydrazide (isoniazid) from nicotinic acid hydrazide by using the Craig distribution (*J. Biol. Chem.*, 1943, **150**, 33) on 50 mg with 25 steps is described. Distribution curves are given. The maximum for the isoniazid is in the tenth step (distribution coefficient $k = 0{\cdot}61$) and for the nicotinic acid hydrazide is in the ninth step (distribution coefficient $k = 0{\cdot}52$) when an *iso*butanol - water mixture is used. A colorimetric method of estimation is required and existing methods are critically reviewed. It was found that the use of Ehrlich's reagent (*p*-dimethylaminobenzaldehyde), under strictly controlled experimental conditions, gave reproducible results.

A Craig distribution in the presence of *iso*butanol - citrate buffer (pH 4·65) was attempted for the detection of *m*-aminophenol in Na *p*-aminosalicylate. The method is greatly affected by pH and it was found that it was not as accurate as other methods already described. R. STERN

2537. **Polarographic determination of leptazol by an indirect method.** V. Parrák (*Československ Farmac.*, 1954, **3** [2], 42–44; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 46,895).—Leptazol is converted into a copper complex, which is then determined polarographically. *Procedure*—To a soln. of leptazol (30 to 120 mg per 100 ml) add 20 to 30 ml of a freshly prepared soln. of $CuCl_2$ (1·25 g of $CuCl_2$ + 10 g of NH_4Cl + 1 g of Na_2SO_3 + water to 100 ml) and cool. After 1 to 2 hr., separate the complex quant. on a 1G4 glass filter and wash, first with 40 ml of a 1 per cent. soln. of acetic acid, and then with ethanol and anhydrous ether. Dissolve the ppt. in a soln. prepared by mixing 4 ml of a 23 per cent. aq. NH_3 soln., 0·2 ml of a freshly prepared conc. Na_2SO_3 soln. and sufficient 0·5 *N* NH_4Cl soln. to make 100 ml. Add 2 or 3 drops of a 0·1 per cent. gelatin soln. and polarograph. Determine the amount of leptazol from a calibration curve for one of the two waves $Cu^{\cdot\cdot} \rightarrow Cu^{\cdot} \rightarrow Cu$.

E. HAYES

2538. **Polarographic determination of 2-phenylquinoline-4-carboxylic acid (cinchophen).** G. Dušinský (*Československ. Farmac.*, 1953, **2** [7–8], 225–226; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No.

50,266).—Cinchophen (**I**) is reduced at the dropping-mercury electrode over a wide pH range. The best supporting electrolyte is 0·1 *N* LiOH soln., in which **I** gives three waves with $E_{\frac{1}{2}} = -1{\cdot}28$, $-1{\cdot}51$ and $-1{\cdot}70$ V (*vs.* the S.C.E.); the first wave is small and with a 1×10^{-3} *M* soln. of **I** the other two waves are combined. The wave height is proportional to the concn. of **I** for the range 5×10^{-5} to 4×10^{-3} *M*. The total wave height indicates two-electron reduction of **I** (Ilkovič equation). The method can be used for the determination of **I** or its salts in the presence of Na salicylate, phenazone or amidopyrine. The error is $\simeq \pm 1$ per cent.
E. HAYES

2539. **Electrophotometric study of tetraethylthiuram disulphide.** V. Parrák (*Československ. Farmac.*, 1954, **3** [3], 87–89; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 46,879).—When 3 ml of a soln. of $CuSO_4.5H_2O$ in methanol (0·0392 g in 100 ml) are added to 0·1 to 0·6 ml of a soln. of tetraethylthiuram disulphide (**I**) in the same solvent (100 to 600 μg of **I**), a stable yellow colour is produced, owing to the formation of the complex—

$$(C_2H_5)_2NC(S)SCuS(S)CN(C_2H_5)_2.$$

The soln. is diluted with methanol to 100 ml and, after 25 min., the colour is measured in a Hilger spectrophotometer with filters H503 and H601 and 1-cm cuvettes. For 0·1 to 0·6 mg of **I**, the relative error is -5 to $+2{\cdot}9$ per cent. In the analysis of tablets, **I** is extracted with CCl_4. E. HAYES

2540. **The change in glucose injections by sterilisation with heating.** S. Takagi and Y. Maekawa (*Japan Analyst*, 1955, **4** [1], 34–36).—Measurements of pH values of various commercial glucose injections by the use of a glass electrode showed values 3·5 to 4·3, much lower than expected. The acid concn. (formic acid and laevulic acid) is measured by a high-frequency titrimeter and found to be $\simeq 10^{-4}$ *N*. It shows a very weak buffer action. These lower pH values appear to be harmless in injections, but it is recommended that Pharmacopoeia Japonica VI should be revised. K. SAITO

2541. **Complexiметric titration in pharmaceutical analysis. VII. Determination of lead.** R. Přibil, J. Čihalík, J. Doležal, V. Simon and J. Zýka (*Československ. Farmac.*, 1954, **3** [3], 84–85; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 46,824).—Lead is determined in $(CH_3COO)_2Pb.3H_2O$, PbO, $2PbCO_3.Pb(OH)_2$, lead plasters and ointments containing lead compounds by treatment with an excess of EDTA (disodium salt) and titration of the excess with $ZnSO_4$ soln. A sample of a pure lead compound (50 mg) or of a lead-containing pharmaceutical preparation (0·2 to 0·5 g) is dissolved in 5 to 10 ml of 0·1 *M* EDTA (disodium salt) soln. and diluted to 20 ml; 5 ml of aq. NH_3 - NH_4Cl buffer soln. (pH 10) and Eriochrome black T indicator (mixture with NaCl, 1 + 200) are added and the solution is titrated with 0·1 *M* $ZnSO_4$ soln. until the colour changes to wine-red. E. HAYES

2542. **Tests for rosin in official pharmaceuticals.** L. Fischer and N. A. Hall (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [3], 150–152).—The cupric acetate test of the U.S.P. XIV is satisfactory for the detection of rosin in cinnamon oil and in juniper tar, and also for the detection of $\not<$ 1 per cent. of rosin in fresh unheated samples of balsam of Peru, balsam of tolu, asafoetida, ipomoea resin and jalap resin; a uniform (1:100) concn. of cupric acetate soln. is recommended. The H_2SO_4 - acetic anhydride test of the U.S. N.F. IX is satisfactory for linseed oil, and (as modified to include preliminary extraction with light petroleum) is more sensitive (0·1 per cent.) and more reliable than the cupric acetate test for aged or heated adulterated samples of balsam of Peru, balsam of tolu, asafoetida, ipomoea resin and jalap resin. A. R. ROGERS

2543. **Polarographic method for the determination of vitamin B_1 [thiamine] in pharmaceutical preparations. Analysis based on curves given by the electro-active forms in alkaline solution.** R. Pleticha (*Československ. Farmac.*, 1953, **2** [5], 149–154; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 49,806).—Sodium hydroxide soln. (0·5 per cent.) is added to a soln. containing $\simeq$ 1 mg of thiamine per ml until the NaOH concn. is 0·1 *N*; a slow stream of an inert gas is passed through until the soln. becomes colourless, and it is then polarographed. Measurement of the total anode - cathode current in the range 0·2 to 1·2 V enables thiamine to be determined with a precision of $\pm$ 3 per cent.
E. HAYES

See also Abstracts 2508, 2520.

Food

2544. **Use of sodium hexametaphosphate in the determination of traces of lead in food.** E. I. Johnson and R. D. A. Polhill (*Analyst*, 1955, **80**, 364–367).—In the method described, the phosphates of the alkaline-earth metals and Mg can be kept in solution suitably for the dithizone extraction of Pb by addition of $Na_6(PO_3)_6$. *Procedure*—Organic matter is destroyed either by wet oxidation or by ashing. The residue is dissolved in 5 ml of water and 10 ml of 5 *N* HCl, and the soln. is boiled and filtered. The filtrate is treated with 2 ml of 25 per cent. ammonium citrate soln. and 10 ml of 10 per cent. $Na_6(PO_3)_6$ soln. and adjusted to the blue - green end-point of thymol blue (pH 9 to 9·5) with aq. NH_3. To the cooled soln., 10 ml of $CHCl_3$ and 1 ml of 10 per cent. KCN soln. are added and, if much Fe is present, 1 ml of 20 per cent. hydroxylamine hydrochloride soln. The vol. of the aq. layer is adjusted to $\simeq$ 50 ml and the liquid is treated in a separator with an aq. soln. of dithizone, prepared by shaking 6 ml of a 0·1 per cent. soln. in $CHCl_3$ with 9 ml of water and 1 ml of 5 *N* aq. NH_3 and centrifuging the separated aq. layer until it is clear. The $CHCl_3$ layer is separated, completion of extraction is confirmed by another extraction, and the combined extracts are treated with 10 ml of dil. HNO_3 (1 + 99) and shaken vigorously. The aq. layer is treated with 30 ml of a soln. prepared by mixing 340 ml of aq. NH_3, 7·5 ml of 2 per cent. Na_2SO_3 soln., 30 ml of 10 per cent. KCN soln. and 605 ml of water, and with exactly 10 ml of $CHCl_3$ and 10 drops of the dithizone soln. The $CHCl_3$ extract is filtered through cotton wool into a spectrophotometer cell and the optical density is measured against $CHCl_3$ at 520 mμ. The result is corrected for a reagent blank prepared in the same way but omitting the sample, and the content of Pb is ascertained from a calibration graph constructed by dithizone extraction of standard solutions of Pb. Preliminary experiments have given some indication that Bi is not so readily extracted with dithizone in the presence of $Na_6(PO_3)_6$ as is Pb; the interference of Bi may thus be reduced. A. O. JONES

2545. **The analysis of industrial glucose.** J. Vollaire-Solva (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [1], 58–66).—A method of analysis of commercial

glucose is described as an alternative to that of Terrier (*Brit. Abstr. C*, 1953, 81). It gives accurate and reproducible results more quickly, but does not distinguish between Terrier's "Dextrin I" (sol. in 95 per cent. methanol) and "Dextrin II" (insol.). *Procedure*—(*a*) *Preparation of soln.* (10 *per cent.*). Into a 250-ml beaker weigh glucose sample (50 g) and water (50 g). Heat in a water bath at 70° C until soln. is complete, cool to 20° C and adjust to the original wt. with water. Weigh accurately 20 g of this soln. and transfer to a 100-ml flask, clarify with Carrez solutions (0·5 ml of each) and dilute to the mark with water. (*b*) *Optical rotation.* Determine the optical rotation of the 10 per cent. soln. in a 2-dm tube at a known temp., using sodium light (≡ rotation due to glucose + maltose + dextrins). (*c*) *Saccharification of dextrins.* Boil 25 ml of the 10 per cent. soln. with 0·5 ml of HCl (sp. gr. 1·19) under reflux for 3 hr.; cool, neutralise with *N* NaOH (methyl orange) and dilute to 500 ml. Determine the reducing-sugar equivalent of the soln. (10 ml) with Luff - Schoorl reagent (25 ml) + water (15 ml) (≡ reducing sugars, maltose + glucose + saccharified dextrins). (*d*) *Reducing sugars.* Determine the reducing sugars in the sample soln. after dilution 1 in 10 by the same method (Luff - Schoorl) (≡ reducing sugars, maltose + glucose). Perform a blank experiment on similar volumes of reagents. (*e*) *Estimation of moisture.* In a tared nickel evaporating dish containing washed ignited sand, intimately mix the sample (≃ 2 g accurately weighed), 1 ml of water, then 30 ml of absolute ethanol. Set the dish aside overnight on top of an oven heated to 100° C. Complete the drying in a vacuum-oven at 70° C and 600 mm pressure in a slow current of dry air. Cool over silica gel, and weigh. Interference due to reducing dextrins can be estimated by the Luff - Schoorl method after fermentation of the maltose and glucose by *Saccharomyces cerevisiae* (van Voorst, *Brit. Abstr. C*, 1949, 350; and Hadorn, *Brit. Abstr. C*, 1951, 265). D. G. FORBES

2546. **Identification of some starches by a selective colorimetric method.** R. Giuliano and M. L. Stein (*Ann. Chim., Roma*, 1955, **45** [2–3], 236–240).—A soln. of the ester of 4-dimethylaminoazobenzene-4′-carboxylic acid and 2-hydroxyethyltrimethylammonium chloride (0·1 per cent. in water) gives distinctive colour reactions with wheat, potato, oat and maize starches. C. A. FINCH

2547. **New nitrogen factor for calculating the protein content of the edible part of herring.** C. H. Brandes and R. Dietrich (*Fette u. Seifen*, 1954, **56** [7], 499–503).—Because of the presence of non-protein nitrogen in the edible part of the herring, the factor 6·25 for converting per cent. nitrogen to protein is too high; analysis of 56 samples, after the non-protein nitrogen has been removed with $Cu(OH)_2$, indicates that the correct factor is 5·72. For this material, a plot of water content against either protein content or fat content gives a straight line; provided that the salt content is less than 0·4 per cent., a single determination of water content enables both the fat (precision ± 0·7 per cent.) and the protein (precision ± 0·45 per cent.) to be calculated. E. HAYES

2548. **Rapid determination of moisture in meat and meat products.** K. Möhler and K. Slevogt (*Fette u. Seifen*, 1954, **56** [1], 46–49).—A weighed sample of homogenised meat or sausage (1 to 2 g) is rubbed for 3 to 5 min. in a glass mortar with 25 ml of "Eluol" (mixture of dioxan and ethylene glycol); the extract is filtered and the dielectric constant of the filtrate is determined. The moisture content is calculated with the aid of a calibration curve obtained with Eluol - water mixtures. For products of high fat content the results are low, but they can be corrected by means of an empirical factor based on the fat content. E. HAYES

2549. **The determination of pectin grade with the Ridgelimeter.** H. C. Lockwood (*Analyst*, 1955, **80**, 315–316).—The "Exchange" Ridgelimeter (Cox *et al.*, *Brit. Abstr. C*, 1944, 133), which gives sag as direct percentage, was recommended as an alternative to the "B.A.R." Jelly Tester (*Analyst*, 1951, **76**, 536). The recommended method has been tested thoroughly and the following observations are made. A boiling pan of 2 to 4 litres is more satisfactory than one of 8 litres. Preparation of the jelly can be simplified. The amount of pectin to give about the same strength as 4·625 g of 100 grade is added with thorough stirring to a soln. of 30 g of sugar in 15 ml of water and, after 5 min., 150 ml of hot water are added and, after another hr., 150 ml of water, and the pH is adjusted to 3·05. The weight of sugar required later is 387 g minus the wt. of pectin. The boiling time should be 8 to 12 min. The ambient temp. for setting is not critical and may be from 7° to 30° C. A standard graph can be used to determine the grade of apple or citrus pectins. The table given relating grade to sag per cent. is prepared from the graph obtained by using a nominal 100-grade apple pectin of actual grade 106 at strengths ranging from 0·51 to 1·28 per cent. w/w, *i.e.*, from two-thirds to one and two-thirds of the standard amount. Typical results are quoted. A. O. JONES

2550. **Determination of dehydracetic acid in fruit juices.** J. Kevei and A. Inczédy (*Magyar Kém. Foly.*, 1954, **60** [4], 106–108; *Referativnŷĭ Zh., Khim.*, 1954, Abstr. No. 50,265).—Fruit juice is extracted with ether and the sum of aldehydes plus dehydracetic acid (**I**) is determined by treating the extract with conc. KOH soln. and measuring the colour formed with salicylaldehyde in a Pulfrich photometer. The colour due to the aldehydes is then determined on the distillate from a sample of neutralised juice, and the amount of **I** present is found by difference. The method permits the determination of 0·02 to 0·50 per cent. of **I**. E. HAYES

2551. **Studies of hop resin components, including the spectrophotometric determination of humulon and lupulon.** J. C. Lewis, J. F. Carson and G. Alderton (*Wallerstein Labs Commun.*, 1955, **18** [60], 33–47).—The term "humulon" is used for the natural mixture of humulone, cohumulone and adhumulone; "lupulon" denotes the mixture of lupulone and analogous compounds. *Procedure*—To 5 g of hand-ground hops sufficient petroleum spirit is added to bring the vol. to 100 ml. After thorough extraction an aliquot is diluted with methanol to a vol. convenient for spectrophotometric reading. This soln. is mixed with 1 per cent. of its vol. of 0·2 *N* NaOH in the absorption cell and the absorbance is read immediately at 355, 325 and 275 mμ. The concn. C_H and C_L of humulon and lupulon, respectively, in mg per litre of the solution measured are given by—

$$C_H = -51{\cdot}56\,A_{355} + 73{\cdot}79\,A_{325} - 19{\cdot}07\,A_{275}$$
$$C_L = 55{\cdot}57\,A_{355} - 47{\cdot}59\,A_{325} + 5{\cdot}10\,A_{275}$$

where A_{355}, A_{325} and A_{275} are the absorbance readings in a 1-cm cell at the wavelengths indicated.
N. E.

2552. **Spectrographic determination of metals in brewing materials and beer hazes.** J. R. Hudson (*J. Inst. Brew.*, 1955, **61** [2], 127–133).—In the preparation for quant. analysis by the carbon-arc cathode-layer technique, the ash from beer or wort (200 ml, preferably freeze-dried before ashing), malt (10 g), or hops (2 g), is fused with K_2CO_3 + Na_2CO_3 (2 g), and the trace metals are concentrated on a matrix of Al_2O_3 (containing $\simeq$ 5 per cent. of Fe_2O_3) by application of the pptn. method of Mitchell and Scott (*cf. J. Soc. Chem. Ind.*, 1947, **66**, 330) to an acid aq. solution of the melt. The concentration of Cu, Al and Fe is effected by the addition to the acid solution of 8-hydroxyquinoline and pure SiO_2 (25 g) and adjusting the pH to 5·0 to 5·2 by the addition of aq. NH_3 and 2 *N* NH_4 acetate (50 ml); in this case, Co is used as an internal standard (*cf.* Farmer, *Spectrochim. Acta*, 1950, **4**, 224). Details are given for qual., semi-quant. and quant. procedures. The concn. in beer hazes of Cu, Fe, Sn, Al, Pb, Ni, V and Mo are very greatly in excess of those found in whole beer.
P. S. Arup

2553. **Extraction of polyphenolic compounds from wine.** J. Amiel, P. Dupuy and M. Nortz (*Compt. Rend.*, 1955, **240** [7], 780–782).—The wine (500 ml) is concentrated to $\simeq$ 150 ml *in vacuo* at $\not>$ 40° C in a slightly reducing atm., and is then diluted to 700 ml by addition of ethanol at 95° C to ppt. salts and pectins. The filtrate is adjusted to pH 9 (aq. NH_3) and the lakes are pptd. by adding 100 ml of ethanol (at 95° C) containing 45 g of neutral Pb acetate, meanwhile stirring and keeping the pH constant at $\simeq$ 9. After decantation, the ppt. is recovered by a double centrifugation, made into a paste with a few drops of ethanol, and is then treated (dropwise) with conc. HCl and ethanol until the mixture is slightly acid. If anthocyanins only are present, the solution is blue to reddish, but if flavones only are present, it is pale yellow and there is also a ppt. of $PbCl_2$. The clear filtrate is stable (apart from slight oxidation of flavones) and can be used for the chromatographic separation of the flavones and anthocyanins. The anthocyanins so extracted are unaltered because their content, as determined by the above procedure, in ethanolic solutions of macerated fruit and leaves of vine is the same as in wine, as determined by the Ribereau-Gayon method. The procedure described above also eliminates interference caused by fluorescence of impurities during u.v. spectroscopy.
W. J. Baker

2554. **Oil determination of oilseed. Gravimetric routine method.** S. Troëng (*J. Amer. Oil Chem. Soc.*, 1955, **32** [3], 124–126).—A gravimetric method suitable for routine determination of the oil content of oilseeds is described. The seeds, freed from foreign matter, are dried and $\simeq$ 1 g is accurately weighed and mechanically shaken for 15 to 20 min. in a centrifuge tube with 4 steel balls and 40 ml of pure petroleum spirit (boiling range 96° to 100° C), the temp. being kept at 20° C. The extract (20 ml) is transferred by pipette into tared beakers containing some grains of pumice, the solvent is evaporated and the residue is dried for 2½ hr. at 200° C and weighed. Twelve determinations with four blanks are made in one run. Results are calculated, taking into account the volume increase from oil going into solution, which has been determined by empirical calibration. The method is found to agree with the Soxhlet extraction method and to be accurate, the error being $< \simeq$ 0·30 per cent.
H. A. Fisher

2555. **Application of ultra-violet spectrophotometry to the analysis of fats and derivatives.** S. F. Herb (*J. Amer. Oil Chem. Soc.*, 1955, **32** [3], 153–158).—This review article surveys the applications of u.v. spectrophotometry for the quant. analysis of fats and oils containing dienoic fatty acids after alkali conversion to the conjugated forms. Sources of error encountered in the more commonly used instruments, particularly the effect of slit width, are discussed in detail. Methods for conversion of non-conjugated to conjugated isomers by using 6·5 per cent. KOH - glycol, 11 per cent. KOH - glycerol, 21 per cent. KOH - glycol (macro and micro) and 11 per cent. KOH - glycol (semi-micro) as reagents are described, and their application and limitations are discussed. These alkaline isomerising agents react more slowly with 1:5-diene systems than with the more usual 1:3 and 1:4 systems, and these methods are therefore not generally suitable for fish oils containing 1:5-diene products. Some recently published data on poly-unsaturated acids isolated from marine oils are discussed in relation to the possibility of extending the method to these. In connection with conjugated fatty acids, tung oil and castor oil are considered in some detail. More accurate spectrophotometric constants in the analysis of drying oils, taking into account the presence of *cis*- and *trans*-isomers, are suggested. (56 references.)
H. A. Fisher

2556. **Separation of fats and fatty acids by paper chromatography.** R. Wegmann, P. F. Ceccaldi and J. Biez (*Fette u. Seifen*, 1954, **56** [3], 159–160b).—Higher fatty acid mixtures are chromatographed on paper (Whatman No. 1 or 2, or Durieux 202) impregnated with liquid paraffin (Nujol); the paper is immersed in a benzene soln. of the paraffin, pressed between filter-paper, and dried flat. The acids are applied as a 5 per cent. soln. in ethanol and the mobile phase comprises paraffin-saturated ethanol (80 to 90 per cent.), methanol (60 to 90 per cent.), butanol or propanol. An ascending technique is used and the solvent rises 30 cm in 16 to 18 hr. The spots are detected with a 1 per cent. ammoniacal soln. of $AgNO_3$, followed by ammonium sulphide soln. Acids differing slightly in molecular weight cannot be separated. The R_F value for a given acid depends on the other acids present in the mixture; with natural mixtures of acids, the predominating acid affects the movement of the minor constituent acids and separation is difficult.
E. Hayes

2557. **Paper chromatography in the fat field. XVI. Further experiments on the separation of fatty acids.** H. P. Kaufmann and W. H. Nitsch (*Fette u. Seifen*, 1954, **56** [3], 154–158).—Mixtures of higher fatty acids are separated by chromatography on paper (Schleicher und Schüll 2043b) with paraffin (boiling range 190° to 220° C) as the stationary phase and acetic acid - water mixtures [(70 to 90) + (30 to 10)] as the mobile phase. For development, the paper strips are dried at 120° C and immersed in dil. Cu acetate soln. The excess of Cu acetate is washed off and the paper is immersed in $K_4Fe(CN)_6$ soln. A clean separation of the acids from capric to stearic is achieved. *iso*Propanol (55 to 65 per cent.) impregnated with paraffin is unsatisfactory as a mobile phase.
E. Hayes

2558. **Studies on methods for the determination of lipoperoxides.** J. Glavind and S. Hartmann (*Acta Chem. Scand.*, 1955, **9** [3], 497–508).—Improvements and modifications of the colorimetric indophenol method (*Brit. Abstr. C*, 1950, 325) for determining peroxides in fats and fatty acids are described. The reagent is a 2 per cent. solution of dichlorodihydroxydiphenylamine (**I**) (prepared by reducing 2:6-dichlorophenolindophenol with ascorbic acid) in ethanol. Heating the soln. of **I** with the fat in a mixture of ethanol - benzene - acetic acid (50:45:5, by vol.) at 70° C for $\simeq$ 20 min. is sufficient to complete the oxidation; $CHCl_3$ can be substituted for benzene in the solvent mixture. Observed extinctions are 1·00 (520 mμ) and 1·02 to 1·03 (530 mμ) for 0·001 milli-equiv. of peroxide per 5 ml of soln. The determination can be made at room temp. in the presence of one drop of 0·1 per cent. w/v $FeCl_3$ in ethanol, whilst inhibition by phospholipids can be avoided by addition of 10 to 20 per cent. of $MgCl_2.6H_2O$ to the solvent mixture (the extinction is then $\simeq$ 1·35). Oxygen should be excluded completely, otherwise high results are obtained. The bleaching effect of phospholipids in the Loftus Hills thiocyanate method (*J. Dairy Res.*, 1946, **14**, 340) was also studied and can be overcome by increasing the NH_4SCN concn. in the final solution to 2 to 5 per cent., especially when determining peroxides in butter, soya-bean oil, or oxidised fats of low triglyceride content. (The fat is dissolved in 5 ml of $CHCl_3$ + 3 ml of ethanol, 2 ml of 30 per cent. NH_4SCN in methanol are added, the soln. is de-aerated for 10 min. with pure nitrogen, one drop of $FeCl_2$ reagent is added and the colours are measured after a few min.; heating at 50° C is unnecessary.) Comparison of the indophenol, thiocyanate and iodimetric methods, with and without exclusion of oxygen, indicate that the thiocyanate procedure described above is preferable, for general use, to the iron-catalysed indophenol method, although the error for both colorimetric methods is $\simeq$ 5 to 10 per cent. The iodimetric method cannot be used for samples having low contents of peroxide. The indophenol method is very suitable for phospholipid samples, even when the peroxide content is high. W. J. Baker

2559. **Trace elements in edible oils.** G. Gorbach and A. Vioque-Pizarro (*Fette u. Seifen*, 1954, **56** [3], 177–180).—A sample of oil (10 g) is weighed into a 30-ml quartz crucible, 0·04 ml of a 25 per cent. ethanolic soln. of $Mg(NO_3)_2.H_2O$ is added and the crucible is heated in a specially constructed heating block, the temp. being raised to 350° C at the rate of 50° C per hr. After 15 hr., when the sample should be completely carbonised, the crucible is heated to 450° C in a muffle furnace until the ash is entirely white. Before the ashing, 0·01 ml of a reference soln. containing 0·01 per cent. of Be and 0·1 per cent. of K (Gorbach and Pohl, *Brit. Abstr. C*, 1952, 416) is added. Two 10-g samples of oil are treated at the same time and the combined ash is dried on a water bath with the aid of an i.r. lamp; the residue is dissolved in 0·01 ml of 3 *N* HCl soln. and used for spectrographic analysis. For Fe, Cr and Mn, the limiting concn. is 0·01 mg per kg, and for Zn, 0·1 mg per kg. E. Hayes

2560. **Determination of chlorides in food fats by measuring the electroconductivity of their aqueous extracts.** O. B. Krayanskiĭ and F. I. Palienko (*Maslob. Zhir. Prom-st'*, 1954, [2], 28–30; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 46,850).—A weighed sample of margarine or butter (5 g) is shaken with 50 ml of water at 50° to 60° C; the soln. is filtered through a moist filter-paper, 10 ml of the filtrate are kept at 20° C for 5 to 10 min. and the conductivity is measured by means of an a.c. bridge system. The concn. of NaCl (y) is calculated from: $y = 0{\cdot}00133 + 48{\cdot}5x + 4400x^2$, where x is the specific conductivity. For fats containing 0·04 to 0·07 per cent. of NaCl, the relative error is < 2 per cent. The results are slightly higher than those obtained by the argentimetric method. E. Hayes

2561. **Detection of adulterants in olive oil by chromatographic methods.** C. Petronici (*Chim. e Ind.*, 1955, **37** [4], 273–275).—Linseed oil added to pure olive oil is determined by absorption chromatography on Al_2O_3. The detection of adulterating substances is based on the different displacement of bands on the alumina column viewed under u.v. light. The appearance of several oils on the absorption column is illustrated in colour. Amounts of extraneous oils < 5 per cent. can be detected, but a quant. analysis is possible only when > 15 to 20 per cent. is present. C. A. Finch

2562. **Determination of iodine values of mixtures of saturated and unsaturated amines obtained from the stearin acids.** O. K. Smirnov and V. M. Bezhentseva (*Zavod. Lab.*, 1955, **21** [4], 414).—The normal methods of determining iodine values give fictitiously high results when applied to unsaturated aliphatic amines, because of replacement of H in the NH_2 groups by halide, *e.g.*, with stearins of iodine value $\simeq$ 5 the corresponding "stearylamines" appear to have iodine values of 16 to 18. It is shown that when the amines are used in the form of their hydrochlorides the NH_2 group is protected and the correct iodine values are obtained by the usual method. The chloroform solution of the "stearylamine" is merely shaken with an 8 to 10 per cent. solution of HCl in ethanol before the addition of the iodine reagent. G. S. Smith

2563. **Determination of L-ascorbic acid by paper chromatography.** V. Šanda (*Československ. Farmac.*, 1954, **3** [3], 79–83; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 50,264).—Ascorbic acid is chromatographed on Schleicher and Schüll No. 602 paper; with 50 per cent. methanol as solvent, the R_F value is 0·7 to 0·8, and with water - *n*-butanol - glacial acetic acid (50:40:14·5) it is 0·6 to 0·7. The spots are detected with a 1 per cent. soln. of $AgNO_3$ in 10 per cent. aq. NH_3, 0·005 *N* iodine soln. in 0·4 per cent. starch soln., 0·04 per cent. aq. soln. of 2:6-dichlorophenolindophenol or u.v. light; the area of the spot is proportional to the concn. of ascorbic acid. The method is applicable to lemon juice, white-, red- and black-currants, tomatoes and green peppers. E. Hayes

2564. **Determination of ascorbic acid by potassium iodate.** G. S. Deshmukh and M. G. Bapat (*Z. anal. Chem.*, 1955, **145** [4], 254–256).—The two-stage oxidation of ascorbic acid by potassium iodate is used for the titrimetric determination of ascorbic acid. To 10 ml of the ascorbic acid solution are added 5 ml of 2 *N* HCl and 5 to 10 ml of CCl_4 and the solution is titrated slowly against 0·25 *M* KIO_3. The contents are swirled vigorously after each addition of the oxidant. The liberated iodine is rapidly taken up by the ascorbic acid, the CCl_4 and

aqueous layers remaining colourless during the process. The first end-point is characterised by the appearance of a permanent violet tinge in the CCl_4 layer. The acid concn. is now increased to 5 *N* or above and the titration continued dropwise with continuous shaking. The aqueous layer develops a deep-brown or yellow shade and on further addition of KIO_3 a slow fading of the violet colour of the CCl_4 layer begins. The titration is complete when this colour is discharged. In low acid concn. the ascorbic acid is oxidised by iodine to HI and dehydroascorbic acid (first end-point). On increasing the acid concentration to 5 *N* the HI is oxidised to iodine, which in turn is converted into iodine monochloride (second end-point). The quantity of KIO_3 required up to the second end-point is 1·5 times that necessary for the oxidation of ascorbic acid. Results are accurate and reproducible. R. J. MAGEE

2565. **Action of N-bromosuccinimide on ascorbic acid. New titrimetric method for estimation of ascorbic acid.** M. Z. Barakat, M. F. Abd El-Wahab and M. M. El-Sadr (*Anal. Chem.*, 1955, **27** [4], 536–540).—The method is based on the selective quant. oxidation of ascorbic acid by N-bromosuccinimide. The sample containing $\simeq$ 1 mg of ascorbic acid per ml is treated with 5 ml of 4 per cent. KI, 2 ml of 3 per cent. acetic acid and 2 drops of starch soln., and the soln. is titrated with N-bromosuccinimide soln. (0·1 per cent. w/v) until a permanent blue colour is produced. The method was applied to the assay of pharmaceutical products, biological fluids and edible fruits, in which the error does not exceed $\pm$ 2 per cent. The limiting concn. is approximately 7 μg of ascorbic acid per ml.
G. P. COOK

2566. **Reaction between mercuric chloride and ascorbic acid. Estimation of ascorbic acid.** S. V. Suryanarayana Rao, U. Veereswara Rao and G. Gopala Rao (*Z. anal. Chem.*, 1955, **145** [2], 88–92).—By correct adjustment of pH, using a Walpole buffer mixture (acetic acid - sodium acetate) at pH 4·6 to 5·7, or a McIlvaine buffer mixture (citric acid - Na_2HPO_4) at pH 2·0 to 8·0, it is possible to reduce $HgCl_2$ quantitatively to HgCl in 30 min. instead of 36 hr. as in an earlier procedure. The method is used for the estimation of ascorbic acid, at a pH of 4·0. A. J. MEE

2567. **Vitamin E: analytical procedure for cottonseed and its products.** B. D. Deacon and A. C. Wamble (*J. Amer. Oil Chem. Soc.*, 1954, **31** [7], 284–287).—A method is given for the determination of total tocopherols and α-tocopherol in cottonseed and its products. Solid materials are extracted with hexane in N, the extract being washed with aq. NaOH soln. (1 per cent.) containing $Na_2S_2O_3$ (5 per cent.). A 10-ml aliquot is evaporated in an aluminium cup that fits into a semi-micro molecular still. Samples of oil are weighed directly into the cup. The distillate is dissolved in chloroform, evaporated to dryness and the residue dissolved in ethanol. The colour developed by an aliquot with 2:2′-dipyridyl and $FeCl_3$ is measured at 520 mμ, giving the total tocopherols. Another aliquot of the ethanol soln. is treated with diazotised *o*-dianisidine dihydrochloride in alkaline soln. and the colour is extracted with hexane, the optical density of the soln. being determined at 510 mμ. This gives the γ-tocopherol; the difference from the total tocopherol gives the α-tocopherol.
G. B. THACKRAY

2568. **A new inexpensive method for the estimation of tocopherols.** A. R. S. Kartha, A. S. Sethi and K. C. Gulati (*J. Sci. Ind. Res., B, India*, 1955, **14** [3], 107–110).—Potassium ferricyanide cannot be satisfactorily substituted for 2:2′-dipyridyl in the Emmerie and Engel method (*Rec. Trav. Chim. Pays-Bas*, 1938, **57**, 1351) for the estimation of tocopherols. The drawbacks of the $FeCl_3$-$K_3Fe(CN)_6$ reagent are eliminated if a solution of $Fe_2(SO_4)_3$ containing H_2SO_4 [0·6 g of $Fe_2(SO_4)_3$ in 20 ml of water with 3 ml of conc. H_2SO_4, diluted to 100 ml] is substituted for $FeCl_3$.
G. C. JONES

See also Abstracts 2474, 2543.

Sanitation

2569. **Determination of carbon monoxide in air-pollution studies.** M. Shepherd, S. Schuhmann and M. V. Kilday (*Anal. Chem.*, 1955, **27** [3], 380–383).—The air containing 1 to 25 p.p.m. of CO is drawn through an indicator gel (*Brit. Abstr. C*, 1948, 2) held in special tubes, at definite rates (100 ml per min.) and for definite times. The colour developed after 3 to 4 hr. after exposure is compared with standards. The error is given as 0·1 p.p.m. at the 1 p.p.m. level, and 1 p.p.m. at 10 to 25 p.p.m. concn. D. A. PANTONY

2570. **A colorimetric method for the determination of methyl bromide in air.** G. A. Lugg (*Analyst*, 1955, **80**, 290–295).—In this method the reaction of pyridine solutions of methyl bromide with NaOH is used. The governing conditions, namely the presence of a minimum amount of water, the amount and concn. of alkali and the effect of heat, have been studied. *Procedure*—The sample of contaminated air is taken by drawing $\simeq$ 10 litres through a tube reaching to the bottom of a calibrated Winchester-quart bottle. A 15-ml portion of a pyridine - water mixture (99 + 1) is placed in the bottle, which is then quickly stoppered, and the sides are wetted with the liquid. After not less than 7 hr. the bottle is shaken and drained. To 10 ml of the liquid, 0·5 ml of 0·5 *N* NaOH is added and the mixture is heated for 15 min. at 95° C. To the cooled product 0·5 ml of aq. 2 per cent. gum ghatti is added and the colour is read within 10 min. in a Spekker absorptiometer with an Ilford No. 601 filter against water. Standard graphs are prepared by the same procedure with 0·0-, 1·0-, 2·5-, 7·5- and 10-ml aliquots of a standard soln. of methyl bromide adjusted to 10 ml by addition of 99 per cent. pyridine. Methyl iodide and ethyl bromide and iodide give colours of intensity similar to that of methyl bromide; ethyl chloride and ethylene dichloride and dibromide give colours of much less intensity. Higher aliphatic halides interfere only slightly, if at all. Compounds such as CCl_4, $CHCl_3$, trichloroethylene and tetrachloroethane give pronounced red colours with absorption maxima at 365 and 535 mμ compared with the 420-mμ region of compounds of the methyl bromide type. With suitable modifications the method is probably applicable to other halogenated hydrocarbons that readily form pyridinium compounds.
A. O. JONES

2571. **The determination of dissolved oxygen in water with leuco indigo carmine.** K. Wickert and E. Jaap (*Z. anal. Chem.*, 1955, **145** [5], 338–344).—Leuco indigodisulphonic acid is obtained by the reduction with Zn of an ammoniacal solution of indigodisulphonic acid. This is added to the water

under test and the colour is measured in a photometric cell with a yellow filter. The method has been successfully tried with concn. of oxygen of 3 to 50 μg per litre. Limits of interfering substances are given, together with a critical survey of existing methods for the determination of O in water. R. STERN

2572. **Determination of chlorides in sea water by a simplified potentiometric method.** J. Denamur (*Compt. Rend.*, 1955, **240** [11], 1223–1225).—Quant. comparison of the Mohr - Knudsen colorimetric-titration method for determining chlorides in sea water with the simplified potentiometric-titration method of Deschamps (*Anal. Abstr.*, 1954, **1**, 1512) shows that equal accuracy (within 0·01 per cent.) in both methods is attained provided that the sample used in the potentiometric titration is adjusted to an acetone content of 50 per cent. v/v by addition of a mixture (2 + 1) of acetone and dist. water. The quant. used are preferably sample (15 ml), acetone (30 ml) and water (15 ml). The potentiometric titration should be continued very slowly, dropwise, towards the end-point; there is no need to disturb the ppt. as in the Knudsen procedure. W. J. BAKER

2573. **The use of a differential refractometer for determination of the purity of solid organic compounds, with special reference to gamma benzene hexachloride.** R. Hill and A. G. Jones (*Analyst*, 1955, **80**, 339–346).—The construction of a simple differential refractometer and its application to the determination of γ-benzene hexachloride in samples approaching 100 per cent. purity are described. *Procedure*—The sample (7·5 $\pm$ 0·1 g) is weighed into a 50-ml flat-bottomed flask equipped with a stopper and stirrer, and an equal amount of the pure γ-isomer is put in a similar flask. To each flask 30 ml of the solvent mixture, *viz*, *n*-butyl acetate and *n*-butanol (1 + 1), are added and solution is effected by warming in a water bath at 40° to 50° C. The flasks are then supported in a water bath at 15°C (or between 15° and 2°C below room temp.) and the liquids are vigorously stirred to induce pptn. of fine crystals of excess of the isomer. The liquids are maintained at this temp. for 3 hr. and are stirred for about 10 min. in each hr. The supernatant liquids are then drawn through cotton-wool filters into suitable pipettes, transferred to 2-oz. bottles and set aside for 1 hr. to attain room temp. The refractometer is set to a zero reading with the soln. of the pure standard, which is then removed by means of a pipette and replaced by the sample soln., and the difference in refraction (Δd) is determined. The γ-isomer content of the sample is ascertained from a calibration graph, which is prepared by the same procedure with synthetic mixtures containing 0·5, 1·0, 2·0, 3·0, 4·0 and 5·0 per cent. of impurity, a mixture of the α-, β- and δ-isomers being used as the impurity. The percentage of γ-benzene hexachloride is plotted against Δd. With synthetic samples containing up to 5 per cent. of the other isomers, the impurity content can be determined to within 0·1 per cent. It is essential that the impurities should consist only of the other isomers of benzene hexachloride. A. O. JONES

2574. **Flame-spectrophotometric determination of calcium in potable water supplies.** E. G. Will and B. Schwarzkopf (*J. Amer. Wat. Wks Ass.*, 1955, **47** [3], 253–256).—A new flame-spectrophotometric method of determining small amounts of Ca (sensitivity up to 0·1 p.p.m.) in drinking water is described. Tests were carried out with a suitably equipped Beckman DU spectrophotometer, adjusted to 100 per cent. transmittance for 100 p.p.m. of Ca, at 554 mμ with a hydrogen flame, selector 0·1, slit-width 0·34 mm, O pressure 10 lb per sq. in., H pressure 5 lb per sq. in. Dilutions containing 75, 50, 25, 10 and 0 p.p.m. of Ca in 100 ml were prepared from a standard $CaCl_2$ solution and acidified with 20 per cent. H_2SO_4 to $\simeq$ 0·007 *M*. By plotting percentage transmittance against p.p.m. of Ca it was found that the dilutions fell into their proper places on the working curve. Further tests showed that interfering ions (Na, K, Mg < 100 p.p.m.) had no effect on the CaO diatomic emission, that recovery of Ca was almost 100 per cent. and that the accuracy and speed of the method compared favourably with those of other determinations of Ca. S.C.I. ABSTR.

See also Abstract 2602.

Agriculture and Plant Biochemistry

2575. **Colorimetric micro-estimation of copper in plants by 2:2′-diquinolyl.** M. Coppenet, G. Ducet, J. Calvez and J. Bato (*Ann. Agronom.*, 1954, **5**, 597–600).—The formation of a pink complex between Cu^{+} and 2:2′-diquinolyl is the basis of this method. Hydroxylamine hydrochloride was used to reduce Cu^{++} to Cu^{+}. A dried sample of plant material was oxidised with perchloric and nitric acids and the resulting solution neutralised with KOH. Sodium tartrate, hydroxylamine hydrochloride and *iso*pentanol containing 2:2′-diquinolyl were added; the mixture was thoroughly shaken and, after centrifuging, the alcohol layer was removed and the Cu was estimated colorimetrically. Concn. of Fe, Mn and Zn 10 to 20 times that of Cu did not interfere. NUTRITION ABSTR. AND REV.

2576. **Estimation of phenolic hydroxyl groups in lignin. I. Periodate oxidation of guaiacol compounds.** E. Adler and S. Hernestam (*Acta Chem. Scand.*, 1955, **9** [2], 319–334).—A method of determining free phenolic groups in softwood lignin is based on the rapid oxidative demethylation of guaiacol by sodium periodate with liberation of about 0·9 mole of methanol per mole of guaiacol. The action of periodate on various substances containing one or two guaiacyl nuclei and representing the probable structural principles of lignin have been investigated. Substituents in the positions para and ortho to the phenolic hydroxyl group did not, in general, affect the methanol formation. A few exceptions of minor importance are noted. It is concluded that the amount of methanol (moles of methanol per methoxyl group) obtained on periodate oxidation of softwood-lignin preparations, when multiplied by 1·1, will give the number of phenolic hydroxyl groups per methoxyl group in the lignin preparation examined. O. M. WHITTON

2577. **Polarographic determination of myricitrin.** T. Suzuki and M. Ito (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [11], 1230–1231).—The polarographic reduction of myricitrin (a flavone) was studied in aq. soln. of various pH values, and its possible use in analysis is discussed. Myricitrin is stable for 50 min. in a buffer soln. of pH 10·8 containing either citrate and phosphate, or carbonate and tetraborate. Its wave height ($E_{\frac{1}{2}}$, — 0·92 V *vs.* the S.C.E.) is proportional to the concn. within the range 10^{-3} to 10^{-4} *M*. K. SAITO

2578. **The spectrophotometric identification and determination of parathion.** A. I. Briggs (*Analyst*, 1955, **80**, 279–283).—Parathion (OO-diethyl O-*p*-nitrophenyl thiophosphate) can be determined in ethanolic soln. by direct absorptiometric measurement at 276 mμ and checked by hydrolysis to *p*-nitrophenol and determination of this in alkaline soln. at 408 mμ, making allowance for any free *p*-nitrophenol originally present in the parathion by determining the absorption at 408 mμ before hydrolysis. On the basis of results obtained from mixtures of known composition the following method is suggested. *Procedure*—The optical density of the parathion in alkaline ethanolic soln. is determined at 408 mμ to obtain the concn. of any *p*-nitrophenol present ($\epsilon = 20{,}830$). From the optical density at 276 mμ the concn. of parathion is determined ($\epsilon = 9630$) and corrected for the *p*-nitrophenol present ($\epsilon = 1700$). The sample is then hydrolysed and the optical density of the resulting *p*-nitrophenol is determined at 408 mμ, allowance being made for that originally present, and the concn. thus found is calculated to parathion. Hydrolysis is effected by heating the soln. in 95 per cent. ethanol with 0·1 *N* KOH in sealed ampoules at 100° C for 3 hr. For the determination of parathion in viscera, *n*-hexane yields a clean extract and the concn. can be determined spectrophotometrically at 268 mμ ($\epsilon = 10{,}350$). As a check, the *n*-hexane extract (50 ml) is evaporated to dryness with 0·2 *N* KOH under reduced pressure at 50° C to remove solvent, the residue is dissolved in ethanol and hydrolysed, and the resulting *p*-nitrophenol determined. The spectrophotometric behaviour of parathion before and after hydrolysis serves also for its qualitative identification.
A. O. Jones

2579. **Absorption properties of compounds present in technical parathion and dimethylparathion.** F. Sokol (*Chem. Zvésti*, 1953, **7** [7], 429–438; *Referativnýĭ Zh., Khim.*, 1954, Abstr. No. 46,870).—A study of the u.v. absorption spectra of compounds present in parathion (**I**) shows that the curves of OO-diethyl O-*p*-nitrophenyl thiophosphate (**II**), *p*-nitrophenol (**III**) and OOO-triethyl thiophosphate (**IV**) do not overlap and can be used for the quant. determination of **II**, **III** and **IV**. Of the other substances present in technical **I**, O-ethyl OO-bis-*p*-nitrophenyl thiophosphate is slightly soluble and is precipitated 2 hr. after the preparation of **I**; *p*-nitrophenetole (**V**), OS-diethyl O-*p*-nitrophenyl thiophosphate (**VI**) and OO-dimethyl O-*o*-nitrophenyl thiophosphate (**VII**) occur in insignificantly small amounts. A sample of technical **I** (0·028 to 0·050 g) is dissolved in 50 ml of 96 per cent. ethanol; 3 drops of 20 per cent. HCl are added to 5 ml of this soln. and the absorption spectrum is measured in a 1-cm cuvette over the range 250 to 350 mμ with a Hilger spectrophotometer. The concn. of **IV** is determined by difference. A disadvantage of the method is that mixtures containing **V**, **VI** and **VII** cannot be determined because **II**, **VI** and **VII** have similar absorption curves, and the curve of **V** is close to that of **III**. Any sodium nitrophenoxide present in technical **I** must be converted into **III**. The error for **II** is 0·7, for **III**, 4, and for **IV**, 3 per cent. Similar methods are used for dimethylparathion.
E. Hayes

2580. **Polarographic determination of S-(1:2-dicarbethoxyethyl)-OO-dimethyl dithiophosphate [malathion].** W. H. Jura (*Anal. Chem.*, 1955, **27** [4], 525–528).—A polarographic method for the assay of technical malathion is described. Unchanged diethyl fumarate in the insecticide is determined by measurement of the polarographic wave it gives in acid soln. (0·3 *N* HCl, 30 per cent. ethanol), a medium in which malathion is stable and gives no wave. On hydrolysis of the sample with 0·1 *N* NaOH, disodium fumarate is formed from the diethyl fumarate and the malathion. The polarographic wave of fumaric acid is measured after acidifying the soln. The malathion content is calculated from the difference in the wave-heights of portions of the hydrolysed and the untreated sample.
G. P. Cook

2581. **Residues in crops receiving pre-emergence treatment with *iso*propyl 3-chlorophenylcarbamate.** L. N. Gard, B. O. Pray and N. G. Rudd (*J. Agric. Food Chem.*, 1954, **2** [23], 1174–1176).—The determination is described of the *iso*propyl 3-chlorophenylcarbamate (CIPC) content of six food crops which have received pre-emergence treatment with this herbicide. The method involves extraction of the CIPC with methylene dichloride, concentration by evaporation, hydrolysis of the herbicide to 3-chloroaniline with H_2SO_4 and colorimetric determination of the amine. The results, after correction for interference caused by an unknown plant constituent, vary from apparently slightly negative values for sugar beet (roots) and peanuts to a max. of 0·03 p.p.m. for head lettuce.
D. Bailey

See also Abstract 2476.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

2582. **Circulatory system for spectrophotometric titrations.** D. J. Fricker (*Chem. & Ind.*, 1955, [16], 426).—An apparatus for use in determinations of the Ca murexide end-point with EDTA soln. and Ilford spectrum blue 602 filters is described and illustrated. The system comprises a circulatory pump, consisting of a centrifugal agitator revolving in a cell used for titration, and a flow-through cell connected so as to ensure continuous circuit. The rotor is revolved at $\simeq$ 750 r.p.m., and the liquid, whose level reaches the holes in the rotor, passes from the titration cell, via a bubble trap, through the flow-through cell back to the titration cell; equilibrium is reached in 5 sec. after addition of reagents.
S.C.I. Abstr.

2583. **A method for rapidly transferring a substance on paper to the origin of a chromatogram.** G. F. Gregory (*Science*, 1955, **121** [3136], 169).—A substance separated by paper chromatography can be transferred to the origin of another chromatogram by means of a hair dryer, two flat plates with a 1-in. circular hole in the centre and a beaker. A strip is cut from the first chromatogram with the spot in the centre and one end is cut to form a point so that the strip becomes a transfer wick. The wick is attached to another strip of filter-paper by basket weave or platinum wire and is folded and stapled so that it is self-supporting in the beaker which contains eluting solvent. The beaker is covered with the plates, between which is the paper for the second chromatogram with the point of origin in the centre of the hole, and the wick is adjusted so as just to make contact at this point.

The hair dryer is directed to the origin and the air current regulated so that the required spot rise may be obtained. H. F. W. KIRKPATRICK

2584. **Continuous ascending chromatography—new technique.** H. Fischbach and J. Levine (*Science*, 1955, **121** [3147], 602–603).—A procedure is described for removal of the ascending solvent as it reaches the top of the chromatogram. Any suitable container is fitted with a cap with one or more slits through which the top of the paper chromatogram protrudes as a wick, and the ascending solvent is removed by spontaneous evaporation, artificial draught, or in a few instances by bending the wick so that the solvent runs into a beaker. This procedure is more effective than continuous descending methods in providing separations where R_F values are small.
H. F. W. KIRKPATRICK

2585. **An instrument for the automatic photometric evaluation of paper chromatograms and electropherograms.** H. Eberle (*Naturwissenschaften*, 1954, **41** [20], 479).—The light from an u.v. lamp passes in one direction through the paper and on to a photocell and in the opposite direction through a moving wedge-shaped slot and on to a second photocell. Automatic recording takes place on the null adjustment of the cells, which follows the movement of the wedge; 10 cm of strip are read per minute. By employing suitable filters, fluorescent zones can be scanned as well as ordinarily stained material. E. KAWERAU

2586. **An improvement in van Slyke's apparatus for the manometric determination of blood gases.** N. Zöllner and E. Zeilinger (*Naturwissenschaften*, 1954, **41** [18], 423).—The extraction chamber of the apparatus has been replaced by one of similar overall dimensions, but heart-shaped in outline. This shape forces the blood into turbulent motion during shaking and thus shortens the extraction time. Gases are fully shaken out in 3 min. at 140 to-and-fro movements per min., whereas 7 min. are required for complete extraction by the old chamber at this rate. E. KAWERAU

2587. **Modification of the Conway diffusion unit.** K. Urich (*Naturwissenschaften*, 1954, **41** [19], 457).—The error that is introduced by the necessity of opening the lid of the unit is eliminated by the use of a hole (1 mm in diameter) in the lid. It is placed near the edge so that the tip of the pipette touches the wall of the unit. The hole is closed with a small glass slide that has been greased.
E. KAWERAU

2588. **Analytical distillation in miniature columns. Equipment and operation.** J. C. Winters and R. A. Dinerstein (*Anal. Chem.*, 1955, **27** [4], 546–550).—By the use of proper controls and accessories, such as closely controlled power supplies for the distillation-flask heater, a receiving system that avoids mixing the fractions and an efficient vacuum system, miniature distillation columns can be employed to give separations of 15 to 20-ml samples as satisfactory as those obtainable on a larger scale. K. A. PROCTOR

2589. **A photo-electric drop counter for fraction collecting.** P. F. Halfhide (*Lab. Practice*, 1955, **4** [4], 168–171).—An electronic method of collecting chromatographic fractions is described in which the amounts collected may be varied in steps between 5 and 250 drops. Collection by drops rather than by volume or weight is considered to have certain advantages in that the collecting tubes need not be matched by weight, the uniformity of fractions collected is independent of fraction size, and there is no carry-over from fraction to fraction as the drops fall straight into the collecting tubes. Details are given of the component parts, namely, turntable of Perspex and aluminium operated by a drum and pulley system, counting head incorporating photocell, flashlight bulb and lens, amplifier of conventional design, and counter of which the basis is two "Uniselectors." K. A. PROCTOR

2590. **Gravity-feed fraction collector.** N. E. Topp and D. D. Young (*Chem. & Ind.*, 1955, [16], 426–427).—An apparatus used in ion-exchange chromatography to collect eluate at the rate of 6 litres per 24 hr. is described and illustrated. The column is connected with receiving flasks by an inclined tube fitted with a standpipe for displaced air and with screw clips above each flask. The liquid remaining in the connecting and take-off tubes after removal of samples is measured to allow for corrections in the total vol. collected. The process can be applied at flow rates < 500 ml per hr., but is not recommended for elutions with great variations in density. S.C.I. ABSTR.

2591. **Mercury compression manometer.** M. I. Korsunskiĭ and S. G. Itin (*Zavod. Lab.*, 1955, **21** [4], 501–502).—The manometer is designed for pressures of 0·05 to 1 mm of Hg. It is constructed so that there is no additional volume due to a capillary, as in most instruments. Pressure is calculated from scale values that can be read directly, and no preliminary calibration is required.
G. S. SMITH

2592. **Rapid preparation of mineral-oil mulls.** A. K. Presnell (*Anal. Chem.*, 1955, **27** [4], 571–572).—A simple apparatus for rapid and efficient grinding of mineral-oil mulls for i.r. spectroscopy is prepared as follows: Make a pestle from a borosilicate-glass rod ($\simeq$ 4 in. x $\frac{1}{4}$ in.) and heat one end to form a spherical portion $\frac{1}{2}$ in. in diameter. Accurately align the enlarged portion with the rod. Heat strongly a No. 27 standard-taper borosilicate-glass stopper and press a carbon rod into the flat end to form a depression about $\frac{1}{4}$ in. deep, roughly fitting the pestle. This forms a rough mortar. Mount the pestle in the chuck of a stirring motor and grind, with No. 180 carborundum and water, to give a spherical fit with the mortar. In use the pestle is rapidly rotated in the vertical chuck of a variable-speed stirring motor, and the mortar is moved over its ground surface from below. Unless very small quantities are used, the material being ground is rapidly forced out, and at intervals must be scraped back on to the grinding surfaces. This can be done with a spatula without stopping the motor. Hardened steel could be used instead of glass for very hard materials. Good mulls of some materials can be prepared in less than 15 sec.
K. A. PROCTOR

2593. **Photometric titration assembly for Beckman model DU spectrophotometer.** D. W. Klingman, D. T. Hooker and C. V. Banks (*Anal. Chem.*, 1955, **27** [4], 572).—The modification of the test-tube adaptor assembly of the Beckman DU spectrophotometer for photometric titration is described. No alteration of the instrument proper is required.
K. A. PROCTOR

2594. **Photoconductive detectors for infra-red spectroscopy.** A. S. Young (*J. Sci. Instrum.*, 1955, **32** [4], 142–143).—Details are given of the construction of lead telluride photoconductivity cells for use at liquid-air temp. The cell is constructed by evaporation technique within the double wall of a Dewar cell (3 in. × 1·25 in.). An infra-red transparent window (artificial sapphire) is sealed to the cell. Details are given of the spectral response of such cells. G. SKIRROW

2595. **Manual and continuous recording attachments for the Beckman model DU spectrophotometer.** G. L. Royer, H. C. Lawrence, S. P. Kodama and C. W. Warren (*Anal. Chem.*, 1955, **27** [4], 501–506).—The manual recording attachment described is a point-to-point device by which it is claimed 75 points of a spectral curve can be plotted in 25 min. The automatic continuous attachment records percentage transmittance at all wavelengths through which the instrument is operated. The stability is such that the balance point of 100 per cent. transmittance remained fixed within ± 0·5 per cent. during 18 hr. at a wavelength of 300 mμ with air in the sample and reference beams.

K. A. PROCTOR

Thermal

2596. **Apparatus for rapid determination of the moisture content of materials.** K. N. Chizhova (*Zavod. Lab.*, 1955, **21** [4], 496–497).—The method is based on the rapid heating of a thin layer (2 mm) of the material between two massive hinged electrically heated metallic plates. The material is contained in paper packets. For moisture contents greater or less than 20 per cent., 5- and 4-g samples, respectively, are used, and the material is distributed as uniformly as possible in the packet. The time required for removal of water at say 140° to 160° C is found from preliminary experiments, but it is usually ≃ 1 to 2 min. Results agree to within ± 0·5 per cent. with those obtained by use of the usual drying oven at 105° C. G. S. SMITH

2597. **An isothermal bath for use in the temperature range 200° to 500° C.** W. H. Bridges, J. V. Cathcart and G. P. Smith (*J. Sci. Instrum.*, 1955, **32** [4], 139–140).—A molten mixture of $NaNO_3$ and $NaNO_2$ serves as the bath liquid. The bath temp. is controlled by an electronically balanced Wheatstone bridge operated in conjunction with a platinum resistance thermometer. Fluctuations of ± 0·025° C at 400° C occur over a period of 500 hr. but control to within ± 0·01° C is possible over shorter periods. G. SKIRROW

2598. **Miniature bomb calorimeter for the determination of heats of combustion of samples of the order of 50 mg mass.** W. S. McEwan and C. M. Anderson (*Rev. Sci. Instrum.*, 1955, **26** [3], 280–284).—Constructional details are given of a miniature combustion bomb which has an internal volume of 14 ml and is suitable for 50-mg samples. The bomb is equipped with a co-axial stirrer and a special crucible holder designed to prevent carbon deposition. The energy equivalent of the calorimeter is 312 cal. per °C. G. SKIRROW

2599. **A method for determining the freezing point of biological fluids.** G. R. Hervey (*Analyst*, 1955, **80**, 284–289).—An apparatus is described for determining the freezing points of small volumes of fluid (≯ 0·1 ml), in a range of 0° to −5° C. It comprises an electrical system in which the current from a thermocouple in conductivity water is balanced against that from one in the sample, and the temp. of freezing is determined potentiometrically. Its operation is similar to that of a macro-apparatus, the liquid being cooled to below its freezing point and then seeded with a trace of ice. The apparatus is calibrated against a soln. of KCl of known freezing point or with a standard mercury thermometer. The requirements for accuracy are discussed. A. O. JONES

Electrical

2600. **A magnetic pump for the laboratory.** J. S. George (*J. Sci. Instrum.*, 1955, **32** [4], 148).—By means of external magnets a plunger is impelled along the inside of a cylindrical tube in an oscillatory fashion. A non-return valve is incorporated in the plunger and at each end of the tube so as to ensure unidirectional flow of liquid. A make-and-break circuit to the magnets determines the rate of pumping, and the positioning of the magnet determines the length of stroke. G. SKIRROW

2601. **New method for measuring viscosity.** B. Thirion (*Génie Chimique*, 1955, **73** [2], 37–41).—This electronic device for measuring η makes use of the phenomenon of magneto-striction, *i.e.*, the distortion of certain metals and alloys under the influence of a magnetic field. A strip of magneto-strictive steel is made to oscillate longitudinally by means of a coil surrounding half its length. When the strip of steel is immersed in a liquid of which the η is to be measured, the oscillations are damped and their average amplitude is reduced. The η is measured by determining the power necessary to maintain this amplitude at a constant value. Constructional details are given of this ultrasonic viscometer, which has a precision of ± 2 per cent. up to 2000 centipoises and of ± 5 per cent. from 2000 to 50,000 centipoises. By using a special probe, η up to 500,000 centipoises can be measured. The device is employed in a number of U.S. oil refineries. J. M. JACOBS

2602. **Analyser - recorder for measuring hydrogen sulphide in air.** E. B. Offutt and L. V. Sorg (*Anal. Chem.*, 1955, **27** [3], 429–432).—An instrument is described in which air containing 0 to 100 p.p.m. of H_2S is allowed to impinge on a continuously moving strip of film coated with a buffered (pH 6·7) lead acetate suspension in gelatin. A light beam passing through the film falls on a photo-electric cell and the resulting current is recorded via an electronic potentiometer. The instrument is sensitive to 1 to 2 p.p.m. of H_2S, the response time is 10 sec. and it can be used in hot, dust- and smoke-laden atmospheres. D. A. PANTONY

2603. **Mercury cell for cathodic separation of elements.** D. P. Lazarević (*Anal. Chim. Acta*, 1955, **12** [4], 363–367).—An electrolytic cell is described in which the cathode is a vertical nickel wire, 1 mm in diameter, coated with mercury. The cell holds 20 ml of electrolyte and 8 cm of the wire are immersed. Mercury is fed to the top of the wire from a capillary. The p.d. at the mercury - electrolyte interface causes a change in the surface tension of the mercury, the mercury flows evenly down the wire and its surface is continuously

renewed; this results in a high hydrogen overvoltage and permits the quantitative and speedy deposition of various metals, including Mn.

W. C. JOHNSON

2604. **Separation of traces of manganese by electrolysis at a renewed mercury cathode.** H. Coriou, J. Dirian and J. Huré (*Anal. Chim. Acta*, 1955, **12** [4], 368–381).—The quant. electrolytic reduction of manganous ions is made difficult by their high discharge potential and the ease with which they are oxidised at the anode. The electrolytic cell described has a mercury-pool cathode with a surface area of 1 sq. cm and the mercury is renewed by a continuous stream of drops from a capillary. The anode is a platinum-gauze cylinder of surface area 95 sq. cm. The course of the deposition is investigated with variation of a number of practical factors, and conditions are determined for the quant. deposition of Mn from sulphate and perchlorate solutions. An extensive theoretical treatment is also included.

W. C. JOHNSON

2605. **An easily assembled continuous electrophoresis apparatus.** H. A. Saroff (*Nature*, 1955, **175**, 896–897).—In the apparatus described and illustrated a Pyrex-glass cylindrical jar (8½ in. × 6 in.) supports a sheet of filter-paper (wrapped wet round the outside of the cylinder), the sample container, and the buffer solution (inside the jar) and its levelling system (in an inverted bottle above the jar). The filter-paper makes contact with the buffer-wick, on top of which is placed a glass plate (with a central hole) to ensure good contact between paper and wick and to support the inverted bottle. The usual wick carries the sample solution to the filter-paper. The two electrode-wicks, each comprising a stack of three strips of wet filter-paper (12 in. × ½ in.), are in contact with the paper sheet, their freely-hanging ends dipping into the electrode vessels. Samples are withdrawn from the serrations cut in the filter-paper with wicks of wet cotton-thread (≃ 1 mm in diam.) held in place by surface tension. The whole assembly is covered with a plastic bell-jar. By placing one electrode-wick over the joined edges of the filter-sheet and the other on the opposite side of the cylinder, two samples can be run simultaneously. The procedure is suitable for the separation of amino acids. W. J. BAKER

2606. **Preparation of pressed samples for counting carbon-14-labelled compounds.** W. W. Burr, jun., and J. A. Marcia (*Anal. Chem.*, 1955, **27** [4], 571).—A small inexpensive press for the preparation of solid samples for radioactive determination is described. The mounts so prepared display a smooth surface and appear to be of uniform thickness. A fairly large amount of active material is required and may limit the use of the press.

K. A. PROCTOR

See also Abstract 2306.

ERRATUM.—August (1955) issue, abstract 2081, penultimate line.
For 0·0001 *read* 0·001.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångstrom unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher -e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
critical	crit.
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c.p.s.
decompos -ing, -ition	(decomp.)
density	ρ
density, relative	d or wt. per ml
derivative	deriv.
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
electron-volt	eV
equivalent	equiv.
experiment	expt.
foot, feet	ft.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
horse-power	h.p.
hour	hr.
hydrogen ion concentration	$[H^{\cdot}]$
hydrogen ion exponent	pH
inch	in.
infra-red	i.r.
insoluble	insol.
kilogram	kg
kilovolt	kV
kilowatt	kW
maxim -um, -a	max.
melting-point	m.p.
microcurie	μC
microgram	μg
microlitre	μl
micron	μ
milliampere	mA
millicurie	mC
milligram	mg
millilitre	ml
millimetre	mm
millimicron	mμ
millivolt	mV
minimum	min.
minute (time)	min.
molar (concentration)	M
molecul -e, -ar	mol.
normal (concentration)	N
number	no.
observed	(obs.)
ounce	oz
part	pt.
patent	pat.
parts per million	p.p.m.
per cent. wt. in wt.	per cent. w/w
per cent. wt. in vol.	per cent. w/v
per cent. vol. in vol.	per cent. v/v
potential difference	p.d.
pound	lb
precipitate	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ
relative humidity	R.H.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda$
square centimetre	sq. cm
standard temperature and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition the following symbols are used—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, *e.g.*, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, Cl', SO_4''. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, *e.g.*, ferric iron becomes Fe^{III} and cuprous copper Cu^{I}.

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